INTRODUCTION

: : TO : :

Qualitative Analysis

BY
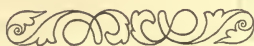
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PREFACE.

THIS book is written primarily for use in the chemical laboratory of the University of Toronto. The laboratory course is designed to complement the work in the lecture room, by making the student familiar with the phenomena treated of in the lectures; and, accordingly, in the present work special attention has been paid to the study of the chemical reaction, and an attempt has been made to introduce in qualitative form the results of the recent advances in the theory of solutions.

With a view of arranging the descriptive matter as concisely as possible, and, at the same time, of developing the powers of observation and comparison in the individual student, the solubilities and colors of the various salts have been presented in tabular form, and the repetition of detailed instruction avoided throughout.

The tables of separation are constructed so as to necessitate continual reference to the text, and are placed with the groups of substances to which they refer; as it is the experience of the authors that when bunched in the usual way, they are made use of to the almost total neglect of the rest of the book.

In conclusion, the authors desire to express their special obligations to the following works :—

> E. J. Chapman : Blowpipe Practice.
> A. Classen : Handbuch d. qual. chem. Analyse.
> W. Ostwald : Die wisse Grundlagen d. anal. Chemic.
> H. v. Pechmann : Anleitung z. qual. chem. Analyse.

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INTRODUCTION

This book is written for the use of students who have already had a certain quantity of instruction in the subject of general Chemistry, who know what is meant by a chemical formula, what qualitative and quantitative information is conveyed by a chemical equation, and who understand the methods employed in the determination of atomic and molecular weights.

They are for the most part introduced to the study of Qualitative Analysis, not to make analysts of them (though some such course as that sketched here forms a necessary part of the education of every professional analyst), but because this course in laboratory work possesses advantages equalled by none other yet devised both in the variety of the substances and the number of the reactions it presents for study, and in the moderate nature of the demands it makes on the time and pocket of the student, on the resources of the laboratory, and on the energies of the instructor. It is not to be denied that these advantages are, to a certain extent, offset by corresponding disadvantages. A large number of bodies is studied, but all from the same point of view ; undue prominence is attached to such compounds (*e.g.*, the insoluble salts) as are convenient for purposes of separation, while, on the other hand, as the reactions are carried out for the most part in aqueous solution, many whole classes of substances—most of the gases, and nearly all bodies decomposed by water—are necessarily excluded from the course ; and even the very reactions most met with, instead of being fair samples of the great majority of chemical reactions, are selected from a type

particularly suited to the necessities of the method of analysis adopted.

From this it follows as a necessary consequence that men whose knowledge of practical chemistry is derived merely from a laboratory course in analysis must form a very one-sided conception of the nature of a chemical reaction, which is all the harder to remove as it is founded on their own experience, and seems to fit the facts too well to need replacement by another. It is with a view of pointing out what is general in the reactions that will be met with in the laboratory, and what is exceptional and due to the fact that chemistry is there studied from the standpoint of the analyst, that this introduction is written.

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If a piece of silver and a piece of copper were melted together, and a chemist were asked to obtain from the alloy (a coin, for instance) the silver and the copper in the pure state, he would proceed as follows:

From tables of the solubilities of the salts of silver and of copper, he knows that while the chloride of silver is very insoluble in water the corresponding cupric salt is quite soluble—the nitrates of both metals are soluble in water. His first step then would be to dissolve the coin in a mixture of nitric acid and water, thus obtaining a solution of the nitrates of the two metals,

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O,$$
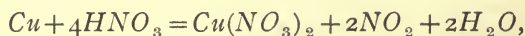
to which he would add hydrochloric acid, thus "precipitating" the silver, i.e., converting it into the insoluble chloride,

$$AgNO_3 + HCl = HNO_3 + AgCl,$$
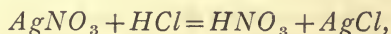
which might be separated from the solution by mechanical means (straining through paper). From this precipitate, after freeing it, by washing, from adhering cupric nitrate solution, he might obtain the silver in the metallic state by

heating it mixed with a little carbonate of soda on a piece of charcoal.

$$2AgCl + Na_2CO_3 + C = 2Ag + 2NaCl + CO_2 + CO$$
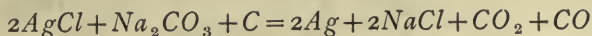
When the silver was thus disposed of, the copper might be obtained from the filtrate by precipitating with potash as the hydrate

$$Cu(NO_3)_2 + 2KOH = Cu(OH)_2 + 2KNO_3,$$
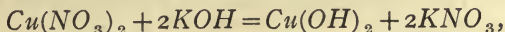
which on heating loses water, passing into the oxide,

$$Cu(OH)_2 = CuO + H_2O,$$
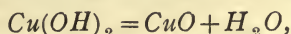
from which, lastly, by heating with charcoal, the copper itself might be prepared.

$$CuO + C = Cu + CO.$$
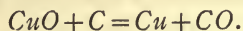
The method of separation here pursued is typical of that followed wherever possible, and, in any particular case, the nearer the operations resemble those just quoted, the better from the point of view of the analyst—and the worse from that of the student of chemistry, who, it goes without saying, is the gainer by variety.

Two peculiarities are common to all the reactions given above. *In the first place*, they are quickly finished ; *in the second*, they are quantitative—*all* the copper and silver are dissolved in the nitric acid ; *all* the silver is obtained as chloride, and this is *all* finally converted into the metallic state, so that the button of silver obtained by the analyst at the end of his work weighs, as near as may be, the same as that originally employed in the manufacture of the coin.

The first feature is common to nearly all reactions of inorganic salts dissolved in water ; the second, on the other hand, is the result of certain special conditions which, therefore, must be fulfilled by all reactions intended as a basis for methods of separation in analysis ; and it is, consequently, of the greatest importance to understand, as far as possible, just what these conditions are, and to learn the effect of each of them separately upon the course of the chemical reaction.

One of the most obvious is the insolubility* of the silver chloride. If it dissolved to any noticeable extent in water, or rather in the solution of copper salts, hydrochloric acid, etc., from which it is to be removed by filtration, then, even if the hydrochloric acid used converted all the silver nitrate into silver chloride, it is evident that only a part of the silver present would be separated in the form of *solid* silver chloride, the rest remaining dissolved and mixed up with the copper in the solution.

There is, however, another very important respect in which this property of the silver chloride affects the reaction ; *for it is very largely owing to the insolubility of this salt that the hydrochloric acid can convert the silver nitrate completely into chloride.* In order to comprehend this latter important proposition it will be necessary to consider a few cases of chemical reaction in which all the substances involved are " soluble": such, for instance, are the two bodies, hydrochloric acid and sodium nitrate, and the two others, nitric acid and sodium chloride, that would be formed from them if they reacted together in solution according to the equation :

$$HCl + NaNO_3 = HNO_3 + NaCl$$
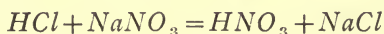
analogous to $HCl + AgNO_3 = HNO_3 + AgCl.$

The only difference between these two cases is that in the latter, if more than an infinitesimal quantity of the " insoluble " silver chloride be formed, it must necessarily be " precipitated," *i.e.*, separated in the solid form ; whereas, in the former, all four bodies are so soluble in water that if fairly dilute solutions be employed no change of the nature represented above can produce a precipitate : and, accordingly, on mixing fairly dilute solutions of the two substances mentioned (hydrochloric acid and sodium nitrate), no precipitate is formed.

Is it, then, fair to say that "nothing happens" on mixing these solutions ? or that the two bodies named " do not react " with each other ? Obviously not. That would be to make the formation of a precipitate the sole criterion of the occurrence

* Short for " very slight solubility " — one litre of water at 18°C. dissolves about 1.7 *mg.* silver chloride. See page 9.

of a chemical reaction. On the other hand, if anything *has* happened, how is one to find it out ? By evaporating the solution and seeing what salt crystallizes out ? Or by adding alcohol and (as, in general, salts are less soluble in water diluted with alcohol than in the same quantity of pure water) thus producing a precipitate? Evidently not, for these expedients would only succeed in reducing the case to one of the former type, depending on the relative solubilities of the various substances involved, while the whole object of the enquiry is to find the laws governing chemical reactions when that disturbing element is removed.

An answer to the question just put may, however, be obtained by studying the " physical " changes which take place on mixing the two solutions. If there be no evolution nor absorption of heat, if no contraction nor expansion, change of color, etc., etc., take place; in short, if all the measurable properties of the mixed solutions be merely the average (properly calculated) of those of the two solutions mixed, it would be a safe conclusion that no reaction had taken place. If, on the other hand, the physical properties of the mixture be intermediate between those of solutions (in the same quantity of water) of hydrochloric acid and of sodium nitrate on the one hand, and of nitric acid and of sodium chloride on the other—which is the actual case—it is fair to infer that the mixture contains not one pair exclusively, but some of each of the four bodies represented by the formulæ, HCl, $NaNO_3$, HNO_3, and $NaCl$; in other words, that a reaction *does* take place between the two first mentioned, but stops short before they are entirely converted into the second pair—that the reaction is " incomplete."

A very striking instance of such a change of physical properties is afforded by one of the reactions used in the analysis of iron salts, viz., the reaction between ferric nitrate and potassium sulphocyanide. The dilute solutions of each of these salts taken separately are almost colorless (that of the iron a little yellowish), while that obtained by mixing them is of a deep blood-red hue, owing to the formation of the deep red ferric sulphocyanide. That the reaction which takes

place when ferric nitrate and potassium sulphocyanide are mixed in solution in the quantities represented in the equation

$$Fe\,(NO_3^{\cdot})_3 + 3KSCN = Fe\,(SCN)_3 + 3KNO_3$$
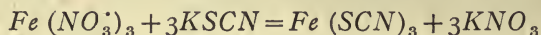
is not "complete," *i.e.*, that all the ferric nitrate employed has not been converted into ferric sulphocyanide, is inferred from the observation that the color of the mixture is not nearly so deep as is that of a solution prepared by dissolving in the same amount of water the quantity of ferric sulphocyanide represented on the right hand side of the equation above. The amount of the red salt formed varies with the temperature and other conditions ; in one case a measurement of the depth of color fixed the quantity of ferric sulphocyanide at thirteen per cent. of what would be present were the reaction "complete."

One of the most important results of the investigations that have been made on this matter is that the solution formed by mixing equivalent quantities of (for instance) hydrochloric acid and sodium nitrate is precisely identical in every respect with that produced from equivalent quantities of nitric acid and sodium chloride,* and the only conclusion that can be drawn from this remarkable fact (which is perfectly general, though a special case is here selected for illustration) is this, that not only can hydrochloric acid react with sodium nitrate according to the equation

$$HCl + NaNO_3 = HNO_3 + NaCl,$$
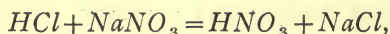
but also nitric acid and sodium chloride, the substances formed by this reaction, can, under suitable circumstances, react together to form again the hydrochloric acid and sodium nitrate from which they themselves were prepared :

$$HNO_3 + NaCl = HCl + NaNO_3$$
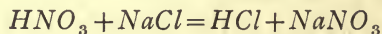
in short, that the reaction of hydrochloric acid on sodium nitrate is "reversible." This may be indicated by replacing the sign $=$ by the sign $\longleftarrow\!\!=\!\!\longrightarrow$ to show that the reaction will proceed *in either direction* according to circumstances.

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*It goes without saying that the same quantity of water must be used in each case.

It is very important to obtain a clear idea of what is involved in the conception of the " reversibility " of a reaction, for it will appear from what follows that this reversibility, instead of being the exception, is the rule even among the reactions met with in the course of analysis. First, then, as to the connection between " reversibility " and " incompleteness." In the case

$$A + B \rightleftharpoons C + D$$
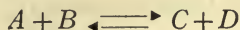
if the substances A and B did react completely to form C and D, the very statement that the reaction between them is reversible implies that these two being present alone would immediately react again to form A and B; and thus the composition of the solution would vary from one extreme—all A and B, to the other—all C and D, the course of the reaction resembling that of a pendulum oscillating about its point of equilibrium. As a matter of fact, however, no such phenomena are met with in chemistry; and if the simile of the pendulum is to be retained at all, the latter must be imagined as provided with a broad vane dipping in glycerine, and prevented by friction from shooting past its point of equilibrium.

Second, as to the causes determining the direction of the reaction: the following, which is a mere restatement of the case just considered, shows that the concentrations of the substances involved is one very important factor. If A and B [and the same holds for C and D] be present alone, they react, and the progress of the reaction involves a diminution of their concentration in the solution and an increase of that of C and D, until a definite relation between the concentrations of the two opposite pairs is arrived at (depending in general on the chemical nature of the reacting bodies), equilibrium is reached, the reaction stops.

There is no question, then, as to what will happen if in the solution at equilibrium the concentrations of *both* A and B be increased (*e.g.*, by dissolving fresh quantities of each of them in the solution)—a reaction will take place in the direction that " uses up " or diminishes the concentration of the substances added, until the former relation between the various concentrations is restored; but what if only *one*, say A, be

added ?   The result is what might be expected, equilibrium is
disturbed, and the ensuing reaction, as in the former case,
serves to diminish the concentration of that substance (*A*)
which was added to the solution.   [The opposite course could
only have resulted in bringing about an explosive reaction
ending in the total disappearance of *C* and *D*; and as this
would be effected by an indefinitely small addition of *A*, it
was very improbable from the outset.]

This influence of concentration has obtained the technical
name of the "action of mass," but it should not be forgotten
that it is not the mass nor the weight of the substances
involved that is of importance, but the *mass per unit volume*
or the concentration.*

The discussion of a concrete example may serve to render
these conceptions more definite.   In the solution formed from
equivalent quantities of ferric nitrate and potassium sulpho-
cyanide—or, what is the same thing, from equivalent quanti-
ties of ferric sulphocyanide and potassium nitrate dissolved in
the same quantity of water—and containing the four salts in
equilibrium with respect to the following reaction :

$$Fe\,(NO_3)_3 + 3KSCN \rightleftharpoons Fe\,(SCN)_3 + 3KNO_3$$
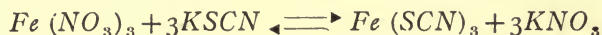
if the concentration of either the ferric nitrate or of the potas-
sium sulphocyanide be increased (*e.g.*, by adding small quanti-
ties of the dry salt, or a drop of the saturated solution of
either) the equilibrium will be shifted and a reaction will
ensue, resulting in the formation of more of the ferric sulpho-
cyanide.   As it is to the latter salt that the solution owes its
red color, it follows that the addition of either of the first-
named salts will deepen the color, and, conversely, addition
of potassium nitrate will render it lighter.   This forms an
easily performed and very striking experiment, which simply
cannot be understood from the other point of view of the
chemical reaction, viz., that it depends on the "relative
affinities" of the substances involved whether or not a reaction
will occur ; and that when one does take place it is quantitative.
From this other standpoint the formation of a red color in

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* In other words, it is the per cent. composition of the solution, not the scale
on which the experiment is carried on, that is the determining factor.

the first instance showed that a reaction had taken place
between the two salts involved; if, on adding more ferric
nitrate, the solution became darker red, that was because the
quantity previously added was insufficient to combine with
the potassium sulphocyanide present. So far, so good; but,
then, what explanation for the deepening in color on addition
of potassium sulphocyanide itself? It *ought not* to deepen!
There was too much potassium sulphocyanide there already!—
The discovery that has removed all these difficulties is just
this, that the "chemical affinity," whatever that very ill-
defined word may really mean, is dependent, among other
things, on the *concentrations* of the reacting substances. This
explains the reversible nature of the reaction, which, again,
necessitates the occurrence of an equilibrium.

In the case just considered it was possible to alter arbi-
trarily, within very wide limits, the concentration of any one of
the four salts involved by adding the substance in question to
the solution and letting it dissolve. But in this very statement
of the possibilities of the case is contained also the necessary
restriction. Most substances will not dissolve in all propor-
tions in water—a few liquids, *e.g.*, nitric and acetic acids, are
completely miscible with water; but in the case of solid sub-
stances and of gases there is always a limit, depending on the
temperature, to the amount that will dissolve on shaking with a
given quantity of solvent; in other words, an upper limit to the
concentration of the solutions that can thus be prepared from
them. In some instances this limiting concentration is high:
water at ordinary temperature will dissolve four times its own
weight of calcium chloride and three-quarters of its weight of
ammonia gas; in others it is low, one hundred parts of water
dissolving seven of mercuric chloride, one-half part of the
chloride of lead, and only 0.00017 of silver chloride. As the
quantity of chloride of lead that will be taken up by a test-
tube full of water is small enough to easily escape notice by the
eye, this and all less soluble substances are in everyday
language spoken of as "insoluble." No salt, however, is
strictly insoluble; the difference between "soluble" and
"insoluble" is one of degree merely, not of kind; and

between the extremes of the chloride of calcium on the one
hand, and the chloride of silver on the other, are to be
found the great majority of the substances met with in the
laboratory.

If, then, one of the salts of a chemical system be "insoluble,"
for instance, the silver chloride in the equilibrium,

$$HCl + AgNO_3 \rightleftharpoons HNO_3 + AgCl,$$
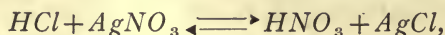
this insolubility will affect its concentration in the solution in
two ways :

(a) The concentration cannot be increased above a certain
    very low limit ;

(b) So long as there is solid silver chloride in contact with
    the solution, the concentration of the silver chloride dis-
    solved will remain constant*;

and the limits thus set to alterations in the concentration
of the silver chloride dissolved have a most important effect
on the course of the reaction.

In the case so often referred to,

$$HCl + NaNO_3 \rightleftharpoons HNO_3 + NaCl,$$
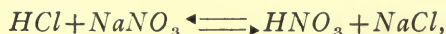
if equivalent quantities of hydrochloric acid and sodium
nitrate be mixed in fairly dilute solution, just about one-half
will be changed into nitric acid and sodium chloride.   If the
nitrate of sodium be replaced by the nitrate of potassium, of
ammonium, of calcium, etc., etc.—in short, by the nitrate of
any metal whose chloride is soluble, the result will be found in
every case to be about the same.   If, however, silver nitrate
be used,

$$HCl + AgNO_3 \rightleftharpoons HNO_3 + AgCl,$$
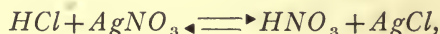
long before half, or, with solutions of ordinary strength, long
before the thousandth part can be converted into the chloride,
the solution is already "saturated" with that salt, *i.e.*, the
concentration of the silver chloride in the solution has
reached its limit, and " precipitation " has begun.   From this
time on, the concentration of the silver chloride in the solution

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* This is strictly true only when the quantities of the other substances in solu-
tion are not too great.

remains constant ; but as that of the nitric acid is increasing, and that of the hydrochloric acid and of the silver nitrate as steadily decreasing—both changes which tend to assist the reverse reaction—it is obvious that at length a state of equilibrium must be reached, in which the nitric acid formed, and the small trace of silver chloride that can dissolve, balance the hydrochloric acid and silver nitrate remaining. Evidently, the less the concentration of the silver chloride, the less can be the concentration of the hydrochloric acid and of the silver nitrate at equilibrium ; and it is thus owing to the extreme insolubility of the former salt that the reaction results as it does in the almost quantitative precipitation of the silver as chloride.

In his power to arbitrarily alter the concentration of the hydrochloric acid, however, the analyst has a means of making the reaction even more complete, and it has long been the practice to add " excess " of the precipitating reagent, *i.e.*, a quantity more than sufficient to combine with all the silver present ;—the explanation of this practical recipe has, however, only comparatively recently been given.

The attention of the student is particularly called to the important argument in the preceding paragraphs, by means of which a theory of " chemical affinity," invented originally to account for the occurrence of incomplete and reversible reactions, is able not only to explain the occurrence of what are, practically speaking, quantitative, non-reversible reactions, but even to give a reason for one of the conditions—excess of the reagent—long known as essential to quantitative precipitation.

The conception of the typical chemical reaction, as reversible and ending in an equilibrium, is of great importance for another reason. The very completeness and non-reversibility of the reactions employed in analytical work, which has just been shown to depend on what might almost be called the " accidental circumstance " of the insolubility of one of the salts involved, was formerly held to be the distinguishing characteristic of a " chemical " as opposed to a " physical "

reaction. Under this latter head were grouped such " changes
of state " as the passage from water to steam, and the
" phenomena of solution," *e.g.*, of salt in water, both being
reversible changes which proceed until an equilibrium is
reached depending on the temperature and on the concentra-
tion (mass per unit volume) of the steam, on the one hand,
and of the salt in solution on the other.

The discovery that chemical reactions proceed according
to the same laws toward the attainment of a similar state of
equilibrium modified by the same factors—among others
temperature, concentration, and the special nature of the
substances involved—has done much to remove this artificial
distinction, which is one of those necessarily met with in the
growth of every inductive science, since the vast mass of
individual phenomena must first be broken up into groups if
any progress is to be made, while an appreciation of the
relations between these various groups can only be arrived at
when the characteristics of each one of them have become
properly understood.

Though a very important factor of the chemical equilib-
rium, the *concentration* of the reacting bodies is not the only
one ; the *temperature* and the *special nature* of the reagents are
equally important, while the storage battery affords an excel-
lent example of chemical action reversed by the influence of
electricity. In this Introduction, however, special attention will
be given only to the concentration and to the chemical nature
of the substances involved, and, unless otherwise specified, all
reactions are supposed to be carried out at constant temper-
ature, and without the intervention of outside electrical forces.

The influence of the " chemical nature " of the various
reacting substances attracted attention at a much earlier
period than did that of their concentrations ; and side by side
with the classification *according to their composition* of the
substances studied under the title of Inorganic Chemistry *

* The compounds containing carbon, which outnumber by far all the others
together, are usually treated of apart under the title " Organic " Chemistry, a name
given to denote their importance in the animal and vegetable kingdom. Carbon
dioxide, however, and the carbonates are, for convenience sake, generally included
among the " Inorganic " compounds.

there has grown up a second system of classification based on their *chemical behavior* : as by far the greater number of the ordinary analytical operations are carried out in aqueous solution, it is no doubt a consequence of this habit of working in the presence of water—which dates back to a period long before the birth of chemical analysis as such —that this second system of classification depends for its foundation upon the behavior of a certain number of the more commonly occurring compounds with that universally employed solvent.

The reaction that serves as a starting point for the system of classification under consideration is that of the neutralization of acids by bases in aqueous solution. Nitric acid reacts with potash according to the equation

$$HNO_3 + KOH = KNO_3 + H_2O.$$
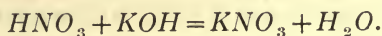
Any substance that can take the place of the nitric acid in this reaction is called an ACID; while any substance capable of replacing the potash is termed a BASE. SALTS are substances formed by the reaction of an acid with a base, according to the equation given above. Those oxides which can be formed from the acids or the bases by the removal of water, or from which by the addition of water the latter may be obtained, have received the name of ANHYDRIDES; while the elements are divided into the two classes of METALS and NON-METALS, according as their hydrates are bases or acids respectively.

Thus the whole classification, which embraces the great majority* of the inorganic compounds, turns on the distinction between Acids, Bases, and Salts. Each of these groups will be shortly considered in turn, the method of subdividing them (still with reference to the "reaction of Neutralization") explained, and, finally, their relations to the "reaction of Hydrolysis," the reverse of the reaction of neutralization, discussed.

* Excluding, however, the most of those decomposed by water, see p. 23. On p. 57 will be found a short account of a group of substances containing Sulphur, which exhibit the same relations *inter se* as those existing between the Oxygen compounds above.

All ACIDS react with potash to form salts (by definition). To "explain" this as due to the "affinity" or "avidity" of the acids for the potash is as much as to say that the acids react with that substance because they want to; similarly, to say that a given substance has "avidity" for bases is evidently merely another way of saying that it is an acid. The use of metaphorical language such as this, however, has been not without benefit to the science; the chemists who pictured to themselves the acids as being endowed with desires, and striving to satisfy them, naturally set themselves the question: "What will happen when two acids want the same base?" and, what is more, were interested enough to institute an experimental enquiry into the subject. In arranging for the contest they did their best to maintain a fair field, saw to it that both acids were present in equivalent quantities, and that no accident, such as the formation of an insoluble salt, should intervene to aid either side; and when they found that, even then, the major portion of the coveted base fell to one of the combatants, they ascribed his victory to his greater "strength" —and thus were the first to give definite meaning to a term which had long been in use, and which will be found of the greatest convenience in describing many of the reactions involving the acids.

To take a particular case, the distinction between a "weak" and a "strong" acid rests on the study of equilibria such as the following :

$$(a) \quad HNO_3 + NaAc \rightleftharpoons HAc + NaNO_3$$
$$(b) \quad HNO_3 + NaCl \rightleftharpoons HCl + NaNO_3$$
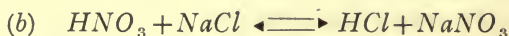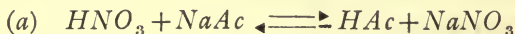
in the first of which nitric and acetic acids, and in the second nitric and hydrochloric acids, are "in competition" for the base soda. If, in each of these two cases, nitric acid and the salt be mixed in equivalent quantities, the state of affairs in the two solutions at equilibrium will be found to be remarkably different—all but a trace of the sodium acetate being converted into sodium nitrate with expulsion of the acetic acid, while very nearly half of the sodium chloride remains undecomposed. The result of these experiments might be

expressed in words by saying that nitric acid has a much greater "avidity" for soda than acetic acid has, and just about the same as hydrochloric acid; but as a great many other bases have been substituted for soda in the reactions formulated above, and as the relative "avidities" of the nitric, acetic, and hydrochloric acids for each of these other bases are found to be practically the same as for soda, it is allowable to speak of nitric acid as being "stronger" than acetic acid and "equal in strength" to hydrochloric, the mention of any particular base not being necessary where all act alike.

The following table gives the relative strengths of some of the acids more frequently met with in the laboratory, compared with that of nitric acid arbitrarily fixed at 10 units, and the figures are the numerical expression of a most important phase of the "chemical nature" of the substances to which they refer. [As recently as 1886 there were no methods available for determining the relative strengths of the various acids, other than those depending on chemical reactions, such, for instance, as those just discussed. Just about that time it was found that the "strength" of an acid in aqueous solution is most intimately connected not only with its whole chemical behavior, but also with a great many of the physical properties of the solution itself, and since then a quantitative theory has been elaborated to connect the physical with the chemical phenomena, by means of which, from a measurement of the melting point, freezing point, electrical conductivity, etc., of the solution of an acid, the numerical value of its strength, as defined above, may be calculated.]

TABLE OF THE RELATIVE STRENGTHS OF THE ACIDS.

10. HCl, HBr, $HClO_4$, $HClO_3$, $HBrO_3$, HNO_3, H_2SO_4, $HSCN$

7.5	HIO_3	1.5	$C_2H_2O_4$.
6.	H_3PO_4	1.	HF
5.5	H_2SO_3, H_3PO_3	0.1	$C_2H_4O_2$
2.5	H_3PO_4	0.02	H_2S
2.	H_3AsO_4	0.01	HCN

The numerical values are approximate only : they hold for decinormal solutions at ordinary temperature and give the relative quantities of the acids present in equilibria, such as (a) and (b) on page 14.

With respect to the BASES, much that has been said of
the acids holds true ; the same distinction between "weak"
and "strong" exists here as there, and the relative strength
of the bases may be measured either by the study of their
reactions, such as, for example,

$$NaOH + KCl \rightleftarrows KOH + NaCl,$$
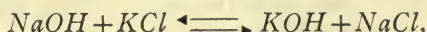
or by measurements of the physical properties of their solutions
in water, just as was the case with the acids. Potash, soda,
and baryta are among the strongest bases ; ammonia in solu-
tion (NH_4OH ?) is much weaker, but the insolubility of the
great majority of the inorganic basic hydrates renders an ac-
curate determination of their relative "avidities" difficult, and
the construction of a table for the commonly occurring bases
analogous to that just given for the acids remains a work for
the future.

Before passing from this discussion of the "strength" or
"avidity" of the various acids and bases to a consideration of
the chemical behavior of the salts, and of the important part
which they play in the reaction of neutralization, one point must
be emphasized, namely, this: it is only in aqueous solution, and
then only if no "insoluble" salt be concerned in the reaction,
that the relative strengths of the acids (or bases) can be the
sole factor determining the course of the reactions in which
they may be involved.   The ease with which the "weak"
phosphoric and boracic acids expel sulphuric, nitric, and
hydrochloric acids from their salts in the blow-pipe reactions,
and the everyday use of hydrogen sulphide in the laboratory
to precipitate the sulphides of the Second Group, show con-
clusively enough that the assistance of heat and of the insolu-
bility or volatility of the products of the reaction may often
enable certain of the weakest among the acids to drive out the
strongest from their salts.   A detailed consideration in this
place of the various typical cases would, however, occasion too
great a break in continuity, and has been relegated to a posi-
tion after the chapter on the First Group ; to be carefully
studied by the student after a little practice has rendered him
familiar with the substances discussed.

The next question is that of the SALTS; and naturally the first question to arise is: " Is there anything in the behavior of this class of compounds analogous to that which underlies the classification of the acids and bases according to their strength ?" The answer to this question is contained—partly, at all events—in what has already been said on the subject of " strength " and "weakness"; and as a clear conception of the meaning of these terms is of great importance in understanding the reactions met with in analysis, attention is particularly directed to the following argument.

In reactions of the type:

$$HS + MW \xrightleftharpoons{} HW + MS$$
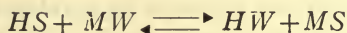
(where HS and HW are two acids, and MW and MS their salts with the metal M), the acid HW, which is present at equilibrium in largest quantity, is called the " weak " acid, as it has been " expelled " from the salt MW by the " stronger " acid HS. Other (metaphorical) reasons might, however, with equal right have been given for the preponderance of the acid HW ; for instance, this—that both acids " had a tendency to be formed," or better, perhaps, " wanted to be free," and that the more astute of the two succeeded in gaining his freedom and imprisoning the other with M. All metaphor aside, that acid which at equilibrium is present in the greatest quantity is the " weak " acid *by definition ;* and the relative " strengths " of any two acids have been found by experiment to be almost independent of the metal M of the last equation. If, however, any one of the salts $MW, M'W, M''W, \ldots MS, M'S,$ $M''S$, etc., experimented with, say $M''W$, for example, had a greater " tendency to be formed," was " weaker " or " more astute " than the others—or, to be more precise, if $M''W$ stood in the same relation to the other salts, with respect to the reaction under consideration, that acetic acid does to nitric acid in the reaction with their sodium salts (page 14), then the quantity of the acid HW formed at equilibrium of the reaction

$$HS + M''W \xrightleftharpoons{} HW + M''S$$
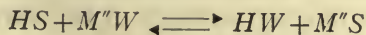
would necessarily be less than in the reactions where these

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other salts were used. In other words, if the various salts differed from one another in the same manner and to anything like the same extent as do the various acids, then the simple relations which have led to the conception of the "strength" of the acids (and the same holds for the bases) would not have existed.

This peculiarity of the Salt solutions is at the bottom of the most striking feature of the whole system of chemical analysis, viz.:—the existence of "tests for lead" and "tests for silver" (and, similarly, "tests for chlorides," "tests for borates," etc.), i.e., of reactions, for the most part involving precipitation, which are common to solutions of all the salts of lead and of silver, etc., respectively. This is possible only because these precipitates are almost without exception produced by adding to the salt solution under examination a reagent solution of *some other salt*, and it would not be so generally the case if solutions of acids were used as the reagents. For instance, in the "test for lead by soluble borates,"

$$Pb\,A + MBor = Pb\,Bor + MA,$$
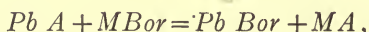
none of the salts represented having any greater "tendency to be formed" than the others, the insolubility of the lead borate ($Pb\,Bor$) determines the course of the reaction, no matter what A and M may be. If, however, instead of a salt of boracic acid the acid itself be used, the direction of the reaction will depend not only on the insolubility of the lead

$$Pb\,A + H\,Bor \rightleftharpoons Pb\,Bor + HA$$
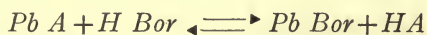
borate, but also on the relative strengths of the two acids involved ;* and, as a matter of fact, in solutions of lead nitrate, no precipitate is produced by boracic acid.

This simplicity in the analytical reactions, caused by the small number of factors on which their course for the most part depends, viz., the relative solubilities of the substances involved, and the relative strength of the various acids (and

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* Other examples page 50 (reactions of Group I), and page 56 (introduction to Group II).

bases), if any be present, is somewhat marred by two circumstances:

First, the exceptional properties of a few salts, mainly derivatives of mercury and cadmium; and

Second, the existence of a class of compounds known as the "double salts," formed from the union of two or more such "simple salts" as have heretofore been discussed.

Mercuric cyanide (soluble in water) furnishes an extreme type of a "weak" salt—if, for the want of a better, this term may be used*: solutions of cyanides convert mercuric salts quantitatively into mercuric cyanide: hydrocyanic acid, though one of the weakest of acids, completely expels nitric acid from combinations with (dyad) mercury: solutions of mercuric cyanide give no precipitates with any of the "reagents for mercury"†—in other words, equilibrium is arrived at in the reaction mentioned only when the system has passed [almost] quantitatively into the state represented on the *right* of the following equations:

$$Hg(NO_3)_2 + 2KCN = Hg(CN)_2 + 2KNO_3$$
$$Hg(NO_3)_2 + 2HCN = Hg(CN)_2 + 2HNO_3$$
$$HgI_2 + 2KCN = Hg(CN)_2 + 2KI$$
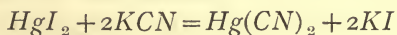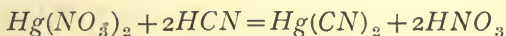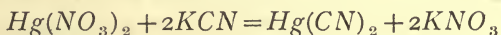
Among the "simple" salts, however, cases resembling even in a slight degree that just considered are extremely rare (cf. mercuric chloride, and mercuric sulphocyanide).

The class of bodies known as DOUBLE SALTS, many examples of which will be met with in the course of analytical work, are important enough to merit a short discussion here. These "double salts" are compounds formed by the union of two or more salts (hereinafter, for convenience sake, termed their "components"), familiar examples being the alums, *e.g.*, $KAl(SO_4)_2 12H_2O$, potassium plumbic iodide $KPbI_3$, etc., etc., to which may be added for the purposes of this discus-

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*The new phys. chem. theory referred to on p. 15 includes mercuric cyanide and the "weak" acids and bases in the group of bodies "slightly dissociated electrolytically in solution."

†The only exception is the precipitation of the extremely insoluble mercuric sulphide.

sion the compounds formed by ammonia with the salts of
silver, copper, etc., *e.g.*, $AgCl\ 3NH_3$

Some of these double salts, for example, alum, may be
dissolved in water and crystallized from that medium; others,
again, are immediately decomposed by water into their com-
ponents, and can only be dissolved in solutions of one of
these; but, as might be expected, their behavior in this
respect is largely influenced by the relative solubilities of the
components and of the double salt itself, and the question to
what extent a double salt, *e.g.*, alum, exists as such in its
solutions can be answered only by comparing the "physical"
properties of the solution in question with those of solutions
of each of the components separately.

Measurements of this nature have been made for a great
many of the double salts, and examples of every degree of
decomposition in solution have been found, from the case of
alum, whose solution appears to contain nothing but a
mixture of the two components, to that of the double salts of
potassium cyanide with the cyanides of iron (potassium ferro-
cyanide and ferricyanide respectively), whose solutions show no
trace of the presence of either of the simple salts from which
they may be prepared. Intermediate between these two
extremes—but rather nearer the ferrocyanide end of the
series—come the ammoniacal silver and copper compounds
above mentioned, and many of the double cyanides; while
nearer the alum end come the double salts of lead chloride
with the alkali chlorides, and those formed by many of the
metallic salts with the alkali citrates and tartrates. In all
the instances considered there is in solution an equilibrium
between the two components and the double salt

$$D \rightleftharpoons C' + C''$$
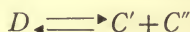
and the influence of concentration or the "action of mass"
is just the same here as in other similar cases. A detailed
discussion of a few examples of the many complications which
may be introduced into the reactions by the existence of
double salts, many of them (those near the ferrocyanide end
of the series) possessed of a "great desire to be formed,"
will be found in the chapter on Reactions of the First Group.

A study of the reaction of Neutralization, to which the preceding five pages have been devoted, besides affording a basis for the classification of the inorganic substances according to their chemical nature, has, in connection with what has been said as to the nature of the chemical reaction itself (pp. 3-12), served to throw a good deal of light on the peculiar features of the reactions employed in chemical analysis, and on the character of the system of chemical analysis itself. A short discussion of the reverse reaction, that of Hydrolysis, *i.e.*, the action of water on some of the salts, forming from them again the acids and the bases from which they were originally prepared, will be found equally useful in defining the relations subsisting between the three classes of which so much has already been said.

To begin with an example of the reaction referred to. The salt, bismuth nitrate, although obtained by dissolving the weak base bismuthous hydrate in nitric acid (and evaporating the solution), is nevertheless decomposed by pure water forming again nitric acid, and the (insoluble) bismuthous hydrate ; that is, the reaction

$$3HNO_3 + Bi(OH)_3 \rightleftarrows 3H_2O + Bi(NO_3)_3$$
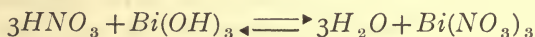
proceeds in either direction, according to the concentration of the nitric acid employed. If the equation just given be written in words instead of in symbols, thus :

Hydrogen nitrate + Bismuth hydrate $\rightleftarrows$ Hydrogen hydrate + Bismuth nitrate
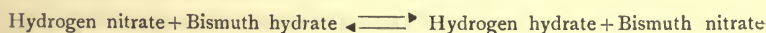
its analogy with the following is at once apparent,

Potassium nitrate + Sodium hydrate $\rightleftarrows$ Potassium hydrate + Sodium nitrate,
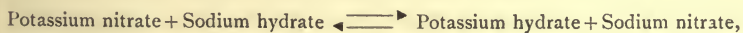
the equilibrium between the reactions of neutralization and hydrolysis may be compared to that which has served to determine the relative strength of the various bases, and in the former case the weak bases bismuthous hydrate and water may be pictured as " contending " for the nitric acid.

From this point of view, it would follow that it is only the salts of weak bases that can be decomposed by water ; but experiment shows that the salts of very weak acids also

readily " undergo hydrolysis." If the explanation for this is to be analogous to that just given, it will be necessary to speak of water as a " very weak acid "—in other words, the same substance must be spoken of in one breath as a base, and in the next as " the very opposite "—an acid. And this is precisely what it is proposed to do, not only in this case, where the only reasons that can be urged are those of analogy, but also in the cases of plumbous, antimonious, stannous, and chromic hydrates and the hydrates of aluminium and zinc, all of which show their right to the name " base " by forming salts with sulphuric acid, and to the name " acid " by forming salts with potash. The fact that so many substances belong equally to both of these classes contributes largely to the formation of correct conceptions as to the relations subsisting between the groups into which a study of the reaction of neutralization has divided the inorganic substances.

The view just taken of the action of water on the salts explains many of the " abnormal " reactions met with in the course of analysis, where, it cannot too often be insisted on, almost all the work is done in aqueous solution. The action of sodium carbonate, for instance, on ferric chloride, instead of forming ferric carbonate according to the equation

$$3Na_2CO_3 + 2FeCl_3 = 6NaCl + Fe_2(CO_3)_3$$
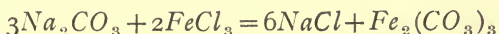
results only in the formation of the hydrolytic decomposition products of that salt, viz., ferric hydrate and carbonic acid ; and the same is true of all reactions which " ought to " lead to salts of the weak bases* with very weak acids, such as carbonic, thiosulphuric, etc., etc. Such salts, consequently, " do not exist," a phrase that probably means nothing more than that all attempts to prepare them have been made in the presence of water, and were consequently doomed to failure from the outset.

But another question arises. If such compounds should some day be prepared by methods which totally avoid the presence of water, would they then be entitled to the name

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*For examples see introduction to Group III.

"salts" as defined above? Is the nitrite of sulphuric hydrate*
a salt? Are the chlorides and sulphides of phosphorus salts?
Certainly not! The definition of a salt, taken in connection with
what has been said of the reaction of hydrolysis, clearly excludes
all bodies that cannot exist in the presence of water, or, at all
events, in the presence of a solution of one of their hydrolytic
decomposition products. And this answer shows what an
important part the behavior of the inorganic substances with
water has played in the classification of them according to
their chemical behavior in general, although this feature was
apparently ignored in the definition of acid base and salt given
on page 13, and although the large group of bodies decomposed
by water, which would have been the first to receive a generic
name if the classification had been carried out from the point
of view of the reaction of hydrolysis, are at present without
one. The products of the hydrolytic decomposition of this
important though nameless class† have been divided into two
groups (acids and bases), and any pair are said to belong to
one and the same group or not, according as the body prepared
from them directly or indirectly by the removal of the elements
of water is or is not decomposed by that substance. No
wonder that some individuals find themselves in both groups!

From this point of view, the anhydrides of the acids and
bases, the acid chlorides (*e.g.*, PCl_5), and bodies such as the
nitrite of sulphuric anhydride already referred to (and the
"mixed anhydrides" of organic chemistry), differ from the salts
only in being more completely decomposed by water; and thus
a study of the reaction of hydrolysis has rendered it possible to
assign to their proper places in the system of classification
adopted a group of substances which, from the very fact that
they are decomposed by water, could take no part in, and con-
sequently could not be classified by, the reaction of neutralization
in aqueous solution.

In conclusion, it may again be insisted on that the student
in the faculty of Arts or of Medicine does not attend the labora-

*Nitrosulphonic acid.

† Which includes many of the "Anhydrides," *e.g.*, sodium oxide, sulphur tri-
oxide, etc.

tory in order to qualify himself for a position as professional analyst, and that he should take advantage of the opportunities afforded him in the laboratory course sketched in this book, not merely by memorizing the scheme of separation adopted nor by acquiring proficiency in the art of "balancing equations," but by endeavoring to become familiar with the nature of chemical reactions and to understand how they may be modified by the special conditions of each experiment. It is hoped that in this attempt he may be materially assisted by the account here given of the course of reactions in solution where none but soluble substances are involved (pp. 4-9) ; of the modifications introduced by the presence of insoluble or volatile compounds (pp. 9-11) ; and, finally, of the system of classification of the more important inorganic substances based on the parts that some of them play in the reactions of neutralization (pp. 13-20) and of hydrolysis (pp. 21-23).

PRELIMINARY INVESTIGATION IN THE DRY WAY.

1. *Behavior on heating alone.*—(*a*) A small portion of the substance is cautiously heated on platinum foil (a piece of tin-type iron will answer in many cases). *Volatilization*—complete or partial—indicates ammonium, mercury, or arsenic compounds. *Blackening* indicates organic substances. If the subject for analysis be a liquid, a couple of drops must be evaporated on the platinum foil with gentle heat, and the residue treated as above ; if there be no residue on evaporation, all metallic salts are absent.

(*b*) The substance is heated in a dry test-tube. *Colorless drops* condensing on the cool part of the tube indicate in general the presence of water (water of crystallization, etc.). *Odor of ammonia* indicates ammonium compounds ; *red vapors*, nitrates.

2. *"Flame test."*—The substance is introduced into the nonluminous flame of a Bunsen burner on a piece of platinum (or iron) wire.

			crimson..yellow..yellow		
Color of the flame...crimson..yellow. violet..			red	red	green. green
Compounds of....... Li Na K			Sr*	Ca*	Ba* Cu*
					B(OH)₃†

*Better if the substance be heated in the reducing flame of a blowpipe, and moistened with hydrochloric acid, before bringing into the Bunsen flame.

†Best after moistening with sulphuric acid.

All other colors are obscured by the yellow sodium light, which, however, is cut off by cobalt glass or indigo solution ; potassium shows violet red through these screens ; strontium and calcium somewhat similar.

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3. *A bead of borax, on addition of a* (minute) *portion of the substance,* is colored :

In the Oxidation Flame.	Presence of.	In the Reduction Flame.
green (red when hot)......chromium.........green
blue .... cobalt ....blue
blue (green when hot) ....copper.............red
yellow (red when hot).....iron ....green
violet ....manganese........colorless
red brown ....nickel...............grey

A bead of microcosmic salt (phosphor salt), on addition of a minute *portion of the substance,* is colored :

In the Oxidation Flame.	Presence of.	In the Reduction Flame.
green (yellow when hot) chromium...green (yellow when hot)
blue ....cobalt ....blue
blue (green when hot)...copper ......red
yellow..................... ..iron ....yellowish green
violet........................manganese ..colorless
yellow ....nickel.........grey

4. *Behavior on heating with soda on charcoal.—(a) Before the blowpipe.* A small quantity of the powdered substance is mixed intimately with from four to six times as much anhydrous carbonate of soda (sodium bicarbonate answers as well), moistened with a drop of water, placed in a small hollow in a block of charcoal and heated in the reducing flame of the blowpipe till all is melted.

Deflagration : nitrates, chlorates, perchlorates, iodates, etc.
Odor of garlic : arsenic.

Sodium sulphide is formed (the fused mass, if moistened with water and brought on a silver coin, stains the latter black): All sulphur compounds.

A metal is reduced with or without formation of an incrustation of oxide in front of the flame.

Metal.	Presence of.	Incrustation.
White, bright malleable specks...tin		....
" " "	..silver	....

Metal.	Presence of.	Incrustation.
Red, bright malleable specks. ...copper		....
Grey, magnetic powder...... ..iron		....
" " " ....cobalt.....		....
" " " ....nickel		....
Bright brittle globule ....antimony..white, volatile.		
" " " bismuth ...brown yellow, non-volatile.		
Bright malleable globule........lead......yellow (hot), white (cold).		
" " " ....zinc ......white.		
" " " ....cadmium..brown-red.		

(b) *Bunsen's method of Reduction :* A strip of filter paper about 8 cm. long and 1 cm. wide is rolled tightly together and dipped for about half its length into melted soda crystals. A small particle of the substance is mixed on the palm of the hand with melted soda (use a penknife), and a little of the mixture placed on the tip of the prepared roll of paper. It must first be carbonized in the upper oxidation flame of a Bunsen burner, then brought into the hottest part of the lower reducing area, and finally let cool in the dark cone of the flame. The reduced metal can be isolated by treating in a porcelain dish with water.

5. *Formation of an incrustation on porcelain :* The substance, supported on a stiff fibre of asbestos, is brought into the upper reduction flame (a rather small flame must be used) of a Bunsen burner, a porcelain evaporating dish full of water being held in the upper oxidation area. *White incrustation*, the oxides of arsenic, antimony, zinc ; *brown-yellow*, bismuth ; *yellow*, lead ; *yellowish white*, tin ; *brown-red*, cadmium.

If the dish be held immediately above the asbestos fibre in the upper reducing flame, a metallic incrustation is obtained : *black*, arsenic, antimony, zinc, bismuth, lead, cadmium, tin, *grey* and discontinuous, mercury. By moistening the incrustations on the porcelain with the proper reagents the characteristic reactions of the various substances may be obtained.

NOTE ON THE USE OF THE BLOWPIPE.*

" In subjecting a body to the action of the blowpipe we ' seek : (1) to raise its temperature to as high a degree as

*Prof. E. J. Chapman's " Blowpipe Practice." Toronto : Copp, Clark Co., 1880.

' possible, so as to test the relative fusibility of the substance ;
' or (2) to oxidize it, or cause it, if an oxide, to combine with a
' larger amount of oxygen ; or (3) to reduce it, either to the
' metallic state, or to a lower degree of oxidation.   The first and
' second of these effects may be produced by the same kind of
' flame, known as an oxidating flame (or $O.F.$), the position of the
' substance being slightly different ; whilst the third effect is
' obtained by a reducing flame (or $R.F.$), in which the yellow
' portion is developed as much as possible, and the substance
' kept within it, so as to be cut off from contact with the
' atmosphere.

    " An oxidating and fusion flame is thus produced.   The
' point of the blowpipe is inserted well into the flame of the gas
' jet, lamp or candle under use, so as almost to touch the surface
' of the gas burner or wick.   The deflected flame is thus well
' supplied with oxygen, and its reducing or yellow portion
' becomes obliterated.   It forms a long narrow blue cone,
' surrounded by its feebly luminous mantle.   The body to be
' oxidized should be held a short distance beyond the point of
' the cone ; but to test its fusion, it must be held in contact with
' this, or even a little within the flame.   In this position many
' substances, such as those which contain lithia, strontia,
' baryta, copper, etc., impart a crimson, green, or other color to
' the outer and feebly luminous cone.

    " For the production of a reducing flame the orifice of the
' blowpipe must not be too large.   The point is held just on the
' outside of the flame, a little above the level of the burner or
' wick.   The flame, in its deflected state, then retains the whole
' or a large portion of its yellow cone.   The substance under
' treatment must be held within this (although towards its
' pointed extremity), so as to be entirely excluded from the
' atmosphere ; whilst, at the same time, the temperature is raised
' sufficiently high to promote reduction.   As a general rule,
' bodies subjected to a reducing treatment should be supported
' on charcoal."

SOLUTION.

Before proceeding with the analysis in the wet way, the substance under investigation must be brought into solution.

If insoluble in cold water, it may be boiled for some time with a little water in a test-tube; any residue remaining undissolved should be filtered off, and a drop of the filtrate carefully evaporated on foil or on a watch glass; a residue shows that the substance is partially soluble. The filtrate should also be tested with litmus paper.

The part insoluble in water should next be treated with dilute hydrochloric acid, proceeding as above: (if the preliminary examination has shown the presence of lead or silver, this treatment with hydrochloric should be omitted).

If insoluble in hydrochloric acid also, dilute nitric acid must be tried, and, finally, aqua regia (pour conc. hydrochloric acid on the substance, and add a few drops of conc. nitric acid).

If any residue remain after treatment with aqua regia, it may be :

Silver chloride, bromide, iodide, cyanide.

The sulphates of barium, strontium, lead (calcium).

The fluorides of calcium, barium, strontium, magnesium, aluminium.

Silicic acid : the silicates.

Tin dioxide : antimony pentoxide.

Carbon : sulphur, etc.

Of these the *silver salts* may be reduced before the blow-pipe to metal, and this dissolved in dil. nitric acid; the *chloride* and *cyanide of silver* are soluble in ammonia (the cyanide is converted into the chloride by hydrochloric acid). *Lead sulphate* may be dissolved in the basic tartrate or acetate of ammonia, or may be converted into lead sulphide (by warming for some time with ammonium sulphide) washed and dissolved in dil. nitric acid. *Antimonic oxide* dissolves in tartaric acid. *Tin dioxide*, if it has once been thoroughly ignited, can only be brought into solution by melting it with caustic soda in a silver crucible. *The others*

(barium, calcium, and strontium sulphates, and the insoluble fluorides and silicates) must be fused with four times their weight of a mixture of sodium and potassium carbonates, the melted mass powdered, and boiled with water (which dissolves the carbonates, silicates, and fluorides or sulphates of the alkalies), filtered, and then treated with hydrochloric acid to bring the carbonates of barium, strontium, and calcium into solution.

TABLE OF THE SOLUBILITIES OF THE MORE COMMONLY OCCURRING SALTS.*

1. Easily soluble in water.
   Group I. Nitrates and acetates ; fluoride of silver.
   Group IIa. Chlorides, bromides, and iodides of tin ; stannous sulphate ; arsenic acid.
   Group IIb. Nitrates and acetates ; chlorides of mercury, copper, and cadmium ; chloride of bismuth (dec. by much water) ; bromide and iodide of cadmium ; mercuric cyanide ; sulphates of copper, cadmium, bismuth ; cupric chromate.
   Group III. Chlorides, bromides, iodides, sulphates, nitrates, acetates.
   Group IV. and Magnesium. Chlorides, bromides, iodides, nitrates, acetates ; hydrates and sulphides of barium and strontium ; sulphate and chromate of magnesium.
   Alkalies. All salts except the perchlorate, acid tartrate, chlorplatinate and silicofluoride of potassium, and the acid pyroantimonate of sodium.
2. Difficultly soluble in water, soluble in hydrochloric or nitric acids.
   Group I. Silver sulphate ; mercurous sulphate ; lead chloride and iodide (lead chloride is more easily soluble in hot water than in hydrochloric acid).
   Group IIa. Antimonious chloride, bromide, and iodide (dec. by water) ; arsenious acid.
   Group IIb. Bromide and iodide of bismuth ; mercuric chromate.

*Taken from H. v. PECHMANN, *Tafeln zur qualit. chem. Analyse.*

Group IV. and Magnesium. Calcium and strontium hydrates; calcium sulphate (a *little* easier in hydrochloric acid than in water); strontium sulphate (very difficultly soluble); calcium sulphide; calcium and strontium chromates; barium iodate; borate oxalate and tartrate of magnesium.

3. Insoluble in water, soluble in hydrochloric or nitric acids or in aqua regia.

Group I. Oxides, sulphides, phosphates, carbonates; chloride, bromide, iodide, chromate, arsenite and arseniate of silver; mercurous chromate.

Group IIa. Sulphides; stannous oxide; antimonious oxide; antimonyl sulphate; stannic phosphate (insoluble in nitric acid).

Group III. Oxides, phosphates, carbonates, sulphides.

Group IV. and Magnesium. Barium chromate; magnesium oxide; phosphates, borates, and oxalates of barium, strontium, and calcium; carbonates; silicates (with separation of silicic acid); calcium, barium, and strontium tartrates.

4. Insoluble in water; difficultly soluble in acids.

Group I. Sulphate and chromate of lead.

Group IV. and Magnesium. Fluorides.

5. Insoluble in water and acids (see above).

DETERMINATION OF THE BASES.

DIVISION INTO GROUPS.

The first step in the determination of bases in the wet way is the subdivision into groups. According to their behavior toward certain so-called group reagents it is possible to divide the commonly occurring bases, in solutions of their salts, into five distinct groups, as shown in the following table:

GROUPING OF THE METALS.

Remove each Group before testing for the next. For modifications in the presence of phosphates, see p. 101

I. *Add* dilute hydrochloric acid, *a drop at a time, as long as a precipitate is produced ; warm, cool again thoroughly, and filter.*

II. *To the filtrate, or, if Group I. be absent, to the original solution containing hydrochloric acid, add* hydrogen sulphide *in excess, warm and filter.*

III. *Remove excess of hydrogen sulphide from filtrate from Group II. by boiling, add a few drops of nitric acid, and boil again, and then* ammonium chloride *and* excess of ammonia.

IV. *To filtrate from Group III. containing ammonium chloride add* ammonium carbonate *and hydrate, digest with gentle heat (not boiling) for some time, and filter.*

V. The filtrate contains :

PRECIPITATE GROUP I.	PRECIPITATE GROUP II.	PRECIPITATE GR. IIIA.	PRECIPITATE GROUP IV.	GROUP V.
Lead, $Pb\,Cl_2$, white	Arsenic, As_2S_3, yellow	A { Aluminium, $Al\,(OH)_3$, white	Barium, $Ba\,CO_3$, white	Magnesium salts
Silver, $Ag\,Cl$, white	Antimony, Sb_2S_3, orange	Chromium, $Cr\,(OH)_3$, bluish green	Strontium, $Sr\,CO_3$, white	Ammonium salts
Mercury (ous), $Hg\,Cl$, white	Tin, $Sn\,S$, brown	Iron, $Fe\,(OH)_3$, reddish brown	Calcium, $Ca\,CO_3$, white	Potassium salts
(Separation, *vide* p. 45.)	$Sn\,S_2$, yellow	*To filtrate add* amm. *sulphide.*	(Separation, *vide* p. 109.)	Sodium salts
	Lead, $Pb\,S$, black	PRECIPITATE GR. IIIB.		Lithium salts
	Bismuth, Bi_2S_3, black	B { Manganese, $Mn\,S$, flesh colored		(Separation, *vide* p. 116.)
	Copper, $Cu\,S$, black	Cobalt, $Co\,S$, black		
	Cadmium $Cd\,S$, yellow	Nickel, $Ni\,S$, black		
	Mercury (ic), $Hg\,S$, black	Zinc, $Zn\,S$, white		
	(Separation, *vide* pp. 67, 77.)	(Separation, *vide* pp. 89, 100)		

THE FIRST GROUP.

The metals of this group are distinguished by the great number of insoluble salts that they form. A number of these should be precipitated from pure dilute solutions of lead, silver, and mercurous nitrates respectively—the reagent solutions are too concentrated, and should be diluted with their own volume of water, and about one cubic centimetre of this dilute solution used in each case. Particular attention should be paid to and a record should be kept of the colors, and state of division of these precipitates ; whether they are light, heavy, slimy, gelatinous, granular, or crystalline; how they behave in the light, on heating with water, with "excess" of the precipitating reagent, etc., etc. ; and any special reactions, such as the solution of the "insoluble" silver salts in ammonia and of the lead salts in potash, should also be tried for the first time with material of known composition.

An investigation of this nature should be carried on with pure salts of each metal as it is met with in the laboratory course ; it is only in this manner, and not from the book, that the necessary personal acquaintance with the various precipitates, etc., is to be gained.

The following practical hints will be found useful in performing the various operations :

Precipitation.—The reagent should be added in small quantities at a time, and between each addition the precipitate induced to subside by heating and shaking ; this should be repeated until finally a drop of the reagent produces no cloudiness in the clear liquid above the precipitate. Any further addition of the reagent serves only to interfere with the subsequent course of the analysis.

Filtration.—The filter paper should in every case be moistened with distilled water before use. As much as possible of

the liquid in the test tube should be poured on the filter paper before the main part of the precipitate is thrown on. If the liquid come through muddy, it should be poured back on the same filter, and this repeated until a clear filtrate is obtained. If the precipitate has been treated as described under "precipitation," no difficulty should be met with in filtration. Many precipitates, when first formed, are slimy, and stop up the pores of the filter paper ; repeated warming with water and shaking are the best remedies.

Washing the precipitate.—This may be done on the filter paper by successive small portions of water from the wash bottle. The quantity of foreign matter left with the precipitate may be reduced almost in a geometrical ratio by each successive washing, if each fresh addition of water be made only when the last has completely drained away. The washing should be continued until an investigation of the wash-water shows that the object of the washing has been attained. The wash-waters themselves should be thrown away, and not used to dilute the first filtrate.

L E A D . Pb. 205.36.

OCCURRENCE.—*Ores :* galena PbS, cerussite $PbCO_3$, anglesite $PbSO_4$. *Metallurgy :* metallic lead is obtained from galena by first roasting in air to convert part of the sulphide into oxide, and afterwards raising the temperature, when the oxide formed reacts with the undecomposed sulphide to form metallic lead, $2PbO + PbS = 3Pb + SO_2$. It is also obtained from the sulphide by reduction with charcoal or iron. *In commerce :* metal; alloys, *e.g.*, solder, and type-metal; and litharge, PbO; red lead, Pb_3O_4; lead nitrate, $Pb(NO_3)_2$; sugar of lead, $Pb(C_2H_3O_2)_2$; white lead, basic carbonate ; chrome yellow, $Pb\,CrO_4$.

ATOMIC WEIGHT.—*Stoech. fig.* (i) 1568.9126 grm. lead yielded 2509.7366 grm. lead nitrate ; (ii) 1090.6085 grm. lead yielded 1596.9459 grm. lead sulphate. *Specific heat*, 0.0314. *Volatile compounds*, lead chloride, and certain organic compounds, *e.g.*, lead tetra-methyl. *Isomorphous relations*, with

calcium, strontium, barium, magnesium, manganese, zinc, and iron in $MeCO_3$; with strontium and barium in $MeSO_4$; with calcium in $Me_5Cl(PO_4)_3$.

CHEMICAL RELATIONS.—Lead occupies a place near the foot of the fourth column of Mendelejeff's table on the left-hand side of, but not far from, the diagonal line. The compounds in which it acts as a tetrad are, however, very few : the dioxide PbO_2 forms salts (plumbates) analogous to the stannates, and more remotely to the carbonates, while plumbic chloride $PbCl_4$ resembles stannic chloride in being a liquid at ordinary temperatures, and in being decomposed by water, though soluble in hydrochloric acid. The plumbous salts PbX_2, in their solubilities and isomorphous relations, resemble those of calcium, strontium, and barium more than those of the magnesium group ; and though many basic salts of lead are known, and the hydrate dissolves in caustic potash solution, it is nevertheless a much stronger base than stannous hydrate, as may be seen from the stability of the plumbous salts with respect to water, and from the existence of a normal carbonate.

THE COMPOUNDS OF LEAD.

NAME.	Color.	Solubility in 100 parts water.* cold	hot	Remarks.
Acetate ... $Pb(C_2H_3O_2)_2$	white	11 (10°)	42(102°)	Sugar of lead..
Bromide .... $Pb\,Br_2$	white	0.5	3.0	S. ex.
Carbonate. ....$Pb\,CO_3$	white	0.0003	insol.	Soda carb. ppts. $2PbCO_3Pb(OH)_2$
Chloride. ....$Pb\,Cl_2$	white	0.74	5.0	S. ex.
Chromate .....$Pb\,CrO_4$	yellow	insol.	insol.	Insol. chromic acid (cf. Ba).
Cyanide .....$Pb\,(CN)_2$	white	insol.	insol.	S. ex., repptd. on boiling.
Ferricyan $Pb_3Fe_2(CN)_2$	brown	s. sol.	s. sol.	
Ferrocyan. $Pb_2Fe(CN)_6$	white	insol.	insol.	Insol. dil. acids.
Hydrate .....$Pb\,(OH)_2$	white	s. sol.	s. sol.	At 130°, PbO; soln. reacts alk.
Iodide ....$Pb\,I_2$	yellow	0.08	0.5	S. ex., repptd. by much water.
Nitrate .....$Pb\,(NO_3)_2$	white	48 (10°)	139(100°)	
Oxalate. ...... PbC_2O_4	white	insol.	insol.	
Oxide ....$Pb\,O$	yellow	insol.	insol.	Other oxides, Pb_2O_3, Pb_3O_4, PbO_2.
Phosphate ..$Pb_3(PO_4)_2$	white	insol.	insol.	
Sulphate ......$Pb\,SO_4$	white	0.005	s. sol.	S. sol conc. nitric acid.
Sulphide ....$Pb\,S$	black	insol.	insol.	Least soluble salt of lead.
Sulphocyan..$Pb(SCN)_2$	yellow	insol.	insol.	Basic upon boiling.
Thiosulph.... $Pb\,S_2O_3$	white	sol.	dec.	Forms PbS upon boiling.

*For solubilities in salt solutions, etc., see page 50.

Lead is a bluish-white, soft, malleable metal, $sp.gr.$ 11.38, $m.p.$ 334°C. Tarnishes in air at ordinary temperatures from formation of plumbous oxide Pb_2O. Easily soluble in dilute nitric acid, with evolution of nitric oxide NO, slightly soluble in conc. sulph. and hydrochl. acids, insol. in dil. sulph. acid.

*Plumbous compounds** PbX_2. Colorless in solution unless the acid be colored.

Plumbous sulphide.—PbS. Hydrogen sulphide from solutions of plumbous salts strongly acidified with hydrochl. acid precipitates brick red or yellow sulphides, $e\,g.$, Pb_2SCl_2, analogous to the basic salts.

Potassium plumbite.—Potash, not in excess, with soluble plumbous salts forms plumbous hydroxide, $Pb(OH)_2$, white, easily soluble in excess of potash to form potassium plumbite, K_2PbO_2: formed also by addition of potash to all insol. plumbous salts except the sulphide and ferricyanide.

. *Potassium plumbate.*—Dilute nitric acid with red lead forms dark brown amorphous plumbic oxide ; also formed by the action of an alkaline solution of bleaching powder on plumbous chloride. Plumbic oxide dissolves in hot conc. potash solution to form potassium plumbate $K_2Pb\,O_3$. Plumbous hydroxide $Pb\,(OH)_2$ in a solution of potassium plumbate produces a yellow precipitate, $Pb_3O_4H_2O$, converted into red lead on heating.

OXIDATION AND REDUCTION.—Lead is converted into plumbous and higher oxides by igniting in air. Plumbous compounds are oxidized to plumbic by the action of nitric acid, bleaching powder, etc. Plumbic compounds with dil. acids or reducing agents such as glycerine, sugar, and oxalic acid, yield plumbous compounds or metallic lead. Plumbous and plumbic solutions deposit metallic lead on aluminium, cadmium, magnesium, zinc, etc. (*Cf.* position of lead in electrochemical series.)

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda, all lead compounds, are reduced to metallic, soft malleable globule.

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*Most insoluble salts of lead may be produced by adding to a soluble lead salt a soluble salt of the required acid, *e.g.*, lead acetate with soda carbonate precipitates lead carbonate (basic).

Borax and microcosmic salt beads: O.F. yellow, hot; colorless, cold. (Platinum wire spoiled in the reducing flame!)

Basic Salts.

These are bodies intermediate in composition between the salts and the bases; on treatment with acids they react, forming the normal salt—hence the name given to the group. Only the weaker bases form basic salts.

The basic salts of lead may be prepared by the following methods (which are also for the most part applicable in the case of other metals):

(i.) By boiling lead salts with the hydrate, filtering hot and allowing to crystallize; the basic nitrate $Pb(NO_3)_2$. $Pb(OH)_2$ may be obtained in this manner in long needle-like crystals.

(ii.) By adding to the solution of a lead salt, potash, in quantity insufficient to convert it altogether into the hydrate:— the hydrate formed reacts with the unaltered salt.

(iii.) By treating many insoluble salts of lead with ammonia or with potash in quantity insufficient to dissolve the salt; *e.g.*, red basic chromate of lead, from the yellow chromate. The reaction ends in an equilibrium between ammonia and the normal salt on the one hand, and the basic salt and the salt of ammonia on the other.

(iv.) From the salts of lead with weak acids, by hydrolysis; lead carbonate, for instance. This mode of preparation, like (ii.), may be considered as due to a secondary reaction between the unaltered salt, and the base formed by hydrolysis.

These salts are often obtained in the form of amorphous muddy-looking precipitates, whose composition varies according to the mode of their formation; and as continued washing very often converts them entirely into the hydrates (hydrolysis), it is next to impossible to obtain them in a fit condition for quantitative analysis;—to set up chemical formulæ for such indefinite substances would be a mere waste of time. In some few cases, however, notably in that of the basic nitrates of lead, a large series of crystalline salts has been isolated.

It has been proposed to represent these basic salts by "structural formulæ" analogous to those of organic chemistry —thus, instead of $Pb(NO_3)_2 . Pb(OH)_2$, would be written $NO_3 - Pb - OH$, intermediate between $NO_3 - Pb - NO_3$ and $HO - Pb - OH$; instead of $Pb(NO_3)_2 . Pb(OH)_2 . 4PbO$, the structural formula $NO_3 - Pb - O - Pb - O - Pb - OH$; while the formula of " white lead," instead of $2PbCO_3 . Pb(OH)_2$, would become $HO - Pb - O - CO - O - Pb - O - CO - O - Pb - OH$. As the molecular weights of most of these substances are unknown, the question of their formulæ cannot be regarded as definitely settled.

SILVER. $Ag = 107.12$.

OCCURRENCE.—*Ores :* native; silver glance, AgS; pyrargyrite, Ag_3SbS_3; in varying quantities in most specimens of galena. *Metallurgy :* metallic silver is obtained from its ores according to three different processes : either it is alloyed with lead and the lead removed by oxidation, or it is amalgamated with mercury and this removed by distillation, or, lastly, it is brought into solution as a salt, and the metal precipitated by means of copper. *In commerce :* alloys, *e.g.,* silver coin; lunar caustic, $AgNO_3$.

ATOMIC WEIGHT.—*Stoech. fig.* (i) 397.3177 grm. silver chlorate yielded on reduction 298.4230 grm. silver chloride; (ii) 397.3177 grm. silver yielded 1287.7420 grm. silver chloride. *Specific heat,* 0.0570. *Isomorphous relations,* with sodium in Me_2SO_4; with the alkalies in silver alum.

CHEMICAL RELATIONS.—Silver is usually placed in the first column of Mendelejeff's table. Copper, silver, and gold forming a group intermediate in properties between nickel, palladium, and platinum, on the one hand, and zinc, cadmium, and mercury on the other. The similarity of silver to sodium is confined to the formulæ of their salts,—both of the type MX —to the isomorphism of a few of their compounds, and to the existence of a quadrantoxide Ag_4O, and of a silver ultramarine.

The metal resembles copper in being one of the best conductors of heat and electricity, and the cuprous salts in their insolubility and in their power of forming compounds with ammonia are very like the corresponding derivatives of silver. Silver occupies a place among the "noble" metals at the "negative" end of the electro-chemical series (see page 55), and is easily obtained in the metallic state from its salts. With the exception of the nitrate and acetate, all the ordinary salts of silver are insoluble in water; many soluble double salts, however, are known.

THE COMPOUNDS OF SILVER.

NAME.	Color.	Solubility in 100 parts water. cold	hot	Remarks.
Acetate......$AgC_2H_3O_2$	white	s. sol.	s. sol.	
Bromide........$Ag Br$	pale yel.	insol.	insol.	Insol. in ammonia.
Carbonate .....Ag_2CO_3	yel. wh.	0.003	....	Heated converted into oxide.
Chloride ....$Ag Cl$	white	insol.	insol.	sol. ammonia.
Chromate .....Ag_2CrO_4	red brown	s. sol.	s. sol	
Cyanide......$Ag (CN)_2$	white	insol.	insol.	S. ex.
Ferrocyan. $Ag_4Fe (CN)_6$	yel. wh.	insol.	dec.	Heated forms ferricyanide.
Ferricyan .$Ag_3Fe (CN)_6$	red brown	insol.	insol.	
Hydrate.......$Ag OH$?	black	[*vide*	oxide]	Forms oxide on heating.
Iodide.... ....$Ag I$	yellow	insol.	insol.	S. ex.; insol. in ammonia.
Nitrate. ......$Ag NO_3$	white	122	111	
Oxalate ......$Ag_2C_2O_4$	white	insol.	insol.	
Oxide ....Ag_2O	gray brw'n	0.3	....	Other oxides Ag_4O, AgO.
Phosphate......Ag_3PO_4	yellow	insol.	insol.	
Sulphate ....Ag_2SO_4	white	0.5	1.5	
Sulphide..........Ag_2S	black	insol.	insol.	Least sol. silver salt.
Sulphocyan ....$AgSC$	white	insol.	insol.	S ex.
Thiosulph ....$Ag_2S_2O_3$	white	50 (16°)	dec.	S. ex., heated forms sulphide.

Sol. pot. cyan.: all insol. silver salts except sulphide.
Sol. tartrates : carbonate.
Sol. ammonia and in ammon. chlor.: all insol. silver salts except iodide and sulphide.

Silver is a soft, white, lustrous, malleable metal, *sp. gr.* 10.5, *m.p.* 954°*C.* Unoxidized in air at ordinary temperatures unless in presence of ozone : tarnished by hydrogen sulphide and by sulphur dioxide. Dissolves readily in dil. and conc. nitric acid, sparingly in dil. and conc. sulphuric acid and conc. hydrochl. acid ; insol. in dil. hydrochl. acid.

Silver salts, colorless, except where the acid is colored·

Silver thiosulphate $Ag_2S_2O_3$ white, from silver solutions by sodium thiosulphate, decomposes immediately into black silver sulphide.

Ammonia silver salts. — Ammonia dissolves all salts of silver except the sulphide and iodide to form double salts, *e.g.* $(NH_3)_3 (AgCl)_2$, etc. From this solution conc. potash precipitates slowly black fulminating silver, which upon boiling is converted into silver oxide.

ACTION OF LIGHT ON SILVER COMPOUNDS.—Most silver salts under the action of light undergo blackening, probably due to formation of compounds such as Ag_4Cl, Ag_4Br, or metallic silver. Upon the easy reduction of these compounds, especially in presence of certain organic substances, such as cellulose, gelatine, etc., depends the use of the chloride and bromide of silver in photography.

OXIDATION AND REDUCTION.—Silver is deposited as a metallic coating or mirror from neutral solutions by aldehyde, dextrose, Rochelle salts, etc.; also by many metals, *e.g.,* copper, iron, mercury, and zinc.

BLOWPIPE REACTIONS.—*B. B.* on *C.* with carb. soda, all compounds of silver are reduced to a malleable metallic bead.

MERCURY. $Hg = 198.80.$

OCCURRENCE.—*Ores :* native (in small quantities), cinnabar, HgS. *Metallurgy :* metallic mercury is obtained from cinnabar by roasting in air and condensing the vapors ; or by distillation with iron filings. *In commerce :* metal alloys, *e.g.,* dental amalgams; vermillion, HgS ; corrosive sublimate, $HgCl_2$; calomel, $HgCl$.

ATOMIC WEIGHT.—*Stoech. fig.* (i) 380.5744 grm. mercuric oxide yielded 352.4079 grm. mercury ; (ii) 177.1664 grm. mercuric sulphide yielded 152.7450 grm. mercury. *Specific heat,* 0.033. *Volatile compounds :* metal ; mercurous chloride, bromide and iodide ; mercuric chloride, bromide and iodide. *Isomorphous*

relations with magnesium, zinc, calcium, copper, iron, nickel, cobalt, and manganese in $MeSO_4$. K_2SO_4. $6H_2O$.

CHEMICAL RELATIONS.—Mercury occupies a place at the foot of column II. in Mendelejeff's table. It forms two series of salts, mercurous HgX, and mercuric HgX_2, the former resembling in their insolubility the silver and cuprous salts, while a few of the mercuric compounds are isomorphous with the corresponding derivatives of the magnesium group. The metal itself is readily obtained from its salts (*cf.* its position in the electro-chemical series); the chloride, though fairly volatile—*b.p.* 293°*C*—may be boiled with water without decomposition, it is one of the few " weak " salts, using the term in the sense given it in the Introduction. Many basic salts of mercury are known, but no hydrate ; solutions of the mercuric salts react acid to litmus.

THE COMPOUNDS OF MERCURY.

Mercury is a silver-white, lustrous, liquid metal, *sp.gr.* 13.59, *m.p.* −39.4°*C.*, *b.p.* 357°*C.* Not oxidized in air at ordinary temperatures ; heated it forms mercuric oxide HgO. Dissolves in dil. nitric acid with formation of mercurous nitrate, in conc. nitric acid with formation of mercuric nitrate, in conc. sulph. acid with evolution of sulphur dioxide, and in aqua regia (three parts of hydrochloric and one of nitric acids) ; insol. in dil. sulphuric and dil. hydrochl. acids.

Mercurous compounds HgX, in solution colorless (except where the acid is colored), mostly insol. in water, soluble in nitro-hydrochloric acid to form mercuric salts.

Mercurous cyanide $HgCN$ white insol., from mercurous nitrate by potassium cyanide, decomposes immediately into mercuric cyanide $Hg(CN)_2$ with separation of free mercury.

Mercurous sulphide is unknown, hydrogen sulphide in solution of mercurous nitrate precipitates mercuric sulphide.

Mercuric compounds HgX_2 colorless in solution, except when the acid is colored.

NAME.	Color.	Solubility in 100 parts cold water	hot water	Remarks.
MERCUROUS.				
Acetate .... $HgC_2H_3O_2$	white	0.8 (15°)	0.8 (15°)	With much water basic salt.
Bromide ....$Hg\ Br$	white	insol.	insol.	
Carbonate.....Hg_2CO_3	grey	insol.	dec.	Heat'd basic carb. and oxide.
Chloride .... $Hg\ Cl$	white	0.0003.	insol.	"Calomel."
Chromate ....(basic)	orange yel.	insol.	insol.	Nitr. ac. forms red Hg_2CrO_4.
Ferrocyan $Hg_2Fe(CN)_6$	wh. (gelat.)	insol.	insol.	
Ferricyan $Hg_3Fe(CN)_6$	red. brown	insol.	insol.	White on standing.
Iodide .... $Hg\ I$	green	s. sol.	insol.	Red on standing.
Nitrate ...$HgNO_3H_2O$	white	(Forms basic salt)		Sol. in a little water.
Oxalate .....$Hg_2C_2O_4$	white	insol.	insol.	
Oxide .... Hg_2O	black	insol.	insol.	No hydrate.
Phosphate ....Hg_3PO_4	white	insol.	insol.	Ppt. first yellow.
Sulphate..... Hg_2SO_4	white	s. sol.	dec.	Dec. by much water.
Sulphocyan..$Hg\ S\ CN$.	white	insol.	insol.	
Thiosulph ....$Hg_2S_2O_3$	white	s. sol.	dec.	S. ex.; dec. to sulphide (ic).
MERCURIC.				
Acetate ......$Hg(C_2H_3O_2)$	white	25 (10°)	100 (100°)	
Bromide ....$Hg\ Br_2$	white	0.4	4	More sol. in alkali brom.
Carbonate ....(basic)	brown	insol.	insol.	
Chloride..........$Hg\ Cl_2$	white	7	54	"Corrosive sublimate."
Chromate .... (basic)	dark red	s. sol.	s. sol.	
Cyanide........$Hg\ (CN)_2$	white	12	53 (100°)	Only s. cyan. of heavy
Ferrocyan....$Hg_2Fe\ (CN)_6$	white	insol.	dec.	Blue on standing. [metals
Ferricyan..$Hg_3(Fe(CN)_6)_2$	yellow	sol.	sol.	
Iodide ....$Hg\ I_2$	yel. or red	Sl. S.	s. sol.	S. ex. "Nessler's solutn."
Nitrate..$Hg\ (NO_3)_2.8H_2O$	white	(basic salts)		Sol. dil. nitric acid.
Oxalate ....$Hg\ C_2O_4$	white	insol.	insol.	
Oxide ....$Hg\ O$	red or yel.	s. sol.	s. sol.	Heated evolves oxygen.
Phosphate......$Hg_3(PO_4)_2$	white	insol.	s. sol.	
Sulphate .. ..(basic)	yel. wh.	0.05	0.16	Sol. dil. sulph. acid.
Sulphide ....$Hg\ S$	black	insol.	insol.	Red on heating.
Sulphocyan ....$Hg\ (SCN)_2$	white	s. sol.	sol.	S. ex."Pharaoh's serpent"

s. ammonia : mercuric carbonate, oxalate, and phosphate.
s. pot. cyan.: all insol. mercuric salts except sulphide.
s. ammon. chlor.: all insol. mercuric salts except sulphide.
S. tartrates : mercurous carbonate, phosphate, and sulphate ; mercuric oxalate.

Mercuric chloride and mercuric cyanide exhibit properties different from those of most other soluble salts of mercury, *e.g.*, (i) they form no basic salts with water, (ii) they may be formed by dissolving mercuric oxide in potassium chloride or potassium cyanide, (iii) the chloride is not precipitated by ammonium oxalate or sodium phosphate, while the cyanide is precipitated

by sulphides only, (iv) from solutions of the chloride sodium bicarbonate precipitates a basic chloride, from those of the nitrate, etc., basic carbonates.

Mercuric iodide HgI_2, from mercuric salts by potassium iodide : the precipitate is first yellow, immediately becoming red. Heated to 150° it suddenly becomes yellow. If upon cooling the yellow mercuric oxide be rubbed with a glass rod, it changes back to the red modification (allotropism, dimorphism).

Mercuric oxide HgO, potash added in small quantities to mercuric solution, produces red brown precipitate of basic oxides ; added to saturation, the normal yellow oxide is produced ; added to strongly acid solutions, soluble double salts are formed.

Mercuric sulphide.—HgS; hydrogen or ammonium sulphide in solutions of mercuric compounds first precipitates double salts, *e.g.*, $HgCl_2HgS.$, varying in color from white to black. (When the precipitation is complete, the precipitate is black.) This is the only metallic sulphide insoluble in dil. nitric acid.

Mercury ammonia compounds :—Many mercurous and mercuric salts react with ammonia to form compounds which may be regarded as substitution products of the latter. Of these may be mentioned *mercurosammonium chloride*, Hg_2ClNH_2, black; by the action of ammonia or mercurous chloride (whence the name "calomel"); soluble in aqua regia ; and *mercurammonium chloride* or "white precipitate," varying in composition from $HgNH_2Cl$ to Hg_2NCl; from neutral mercuric chloride solutions by ammonia ; soluble in hydrochl. acid ; sparingly so in conc. ammonia and ammonia salts.

OXIDATION AND REDUCTION.—It was formerly the custom to speak of the mercurous salts as "salts of the suboxide of mercury," the mercuric compounds being termed "salts of the oxide of mercury." Thus, for example, mercurous chloride was the "chloride of the suboxide," and mercuric chloride the "chloride of the oxide of mercury." Hence to convert the former into the latter was to "oxidize" it, although in

carrying out the actual operation no oxygen need be employed, and, similarly, to remove the chlorine from these bodies was to " reduce " them.   Reduction is the opposite of oxidation.

The following are some of the *oxidizing agents* commonly used in the laboratory :

chlorine water, bromine water ;

nitric, chloric, hypochlorous, chromic, permanganic acids ;

lead dioxide, manganese dioxide (in acid or alkaline solution).

(In the dry way : potassium nitrate and chlorate.)

Reducing agents :

nascent hydrogen ; many metals, *e.g.*, zinc, iron, copper ;
stannous chloride, potassium stannite ; ferrous sulphate ;
hydriodic acid, hydrogen sulphide, sulphur dioxide ;
formic, oxalic, and phosphorous acids, alcohol.

(In the dry way : carbon, potassium cyanide.)

In the case of mercury, mercurous compounds are converted into mercuric by the action of conc. nitric or nitro-hydrochloric acids, also by the action of chlorine, bromine, iodine, etc.   Mercurous cyanide, iodide, and sulphide are transformed spontaneously with separation of free mercury, into the corresponding mercuric compounds.   Mercuric compounds are reduced to mercurous compounds and finally to mercury by the action of stannous chloride, sulphurous acid, sodium thiosulphate, formic and oxalic acids.   Mercuric and mercurous solutions deposit metallic mercury on copper, iron, zinc, etc.

BLOWPIPE REACTIONS, ETC.—*B. B. on C.* with carb. soda. mercury volatilizes from all compounds. In bulb tube with carb. soda, all compounds of mercury are decomposed, free mercury subliming and collecting at the mouth of the tube, where it may be formed into globules by rubbing with a match.

SEPARATION IN THE FIRST GROUP.

Treat the precipitate of the First Group chlorides with hot water, and filter.

(a) Solution: $PbCl_2$. Test for lead.
(b) Residue: $AgCl$, $HgCl$. Treat with warm dilute ammonia, and filter.

Solution: Ammonio silver chlorides.
Residue, black: Mercurosammonium chloride.

To dissolve out the lead chloride from the first group precipitate, one of two plans may be adopted: (a) a small hole may be made in the point of the filter with a sharpened match, and the precipitate washed through into a test tube by a jet of water from the wash bottle, boiled with the water and filtered hot; (b) a small quantity (three or four cubic centimetres) of boiling water may be poured over the precipitate on the filter paper, the filtrate collected in a test tube, boiled, and poured hot over the precipitate, and the process repeated two or three times. In either case, if the filtrate contain lead, the remaining precipitate must be washed again and again with hot water until the washings are quite free from lead (no precipitate with ammonium sulphide); because, if any lead chloride be left undissolved, the addition of ammonia will convert it into a basic chloride, which, being insoluble in water and in ammonia, will remain mixed with the mercurous salt, and will cause trouble with the "confirmatory tests" for the latter.

Similar methods may be employed in removing the silver from the mercury by ammonia.

Confirmatory Tests.

For Lead. The mere fact that a solution on addition of hydrochloric acid gives a white precipitate soluble in hot water, must not be taken as conclusive evidence that the solution

in question contains lead.   If, however, it does contain more than a trace of any salt of that metal, the hot water must give all the reactions of a solution of lead chloride.   See p. 35.

For Silver.—By warming with a solution of grape sugar mixed with potash, the precipitate of silver chloride (produced by nitric acid in the ammonio-silver solution) is converted into metallic silver, which, after being well washed, may be dissolved in a little dilute nitric acid : this solution, freed from excess of nitric acid by boiling, should give the same precipitates as the reagent solution of silver nitrate.   See p. 39

For Mercury.—The black mercurosammonium chloride may be dissolved by warming it with a mixture of ten drops of conc. hydrochloric acid and three of conc. nitric acid (*aqua regia*).   In this solution (which should be boiled to expel excess of acid) the mercury is contained as mercuric chloride (and nitrate), and should be tested for according to page 42.

The student should on no account omit applying these " confirmatory tests," and comparing the precipitates obtained with those from solutions known to contain lead, silver, and mercurous salts respectively ; it is at this stage in the analysis that there is most likelihood of errors in the preceding work being detected.

NOTE. — Precipitates produced by hydrochloric acid in solutions which contain no lead, silver, nor mercurous salts :—

   (i.) Soluble in water : barium chloride, pptd. only by conc. hydrochl. acid.

  (ii.) Soluble in hydrochl. acid : basic chlorides of antimony, bismuth, and tin ; ppts. formed in solutions of zincates, plumbates, etc. ; and in those of some double sulphides.   (See group II.A)

 (iii.) Sulphur, silicic and boracic acid, etc. (see chap. on acids,) arsenious sulphide ; thallious chloride.

REACTIONS OF GROUP I.

In this chapter it is proposed to apply the principles and conceptions discussed in the Introduction, to the special cases met with in the analysis of Group I. In general the reagents, (usually salt solutions) are so chosen that one of the products of their reaction with the salt under investigation is insoluble in water, with the consequence that that substance is more or less completely precipitated. In certain cases, however, the procedure is the reverse of this, as when precipitates are dissolved in excess of the precipitants, or in ammonia, or in acids, etc.; and, finally, there are reactions in which more than one insoluble substance is involved, as, for example, in the precipitation of mercury by copper, and the blackening of the insoluble salts of lead by ammonium sulphide. Each of these cases will be considered separately.

PRECIPITATION. THE DELICACY OF REACTIONS.

In the reagent solution of lead acetate heavy precipitates are produced by soluble chlorides, sulphates, iodides, chromates, sulphides, etc. If, however, the solution provided be diluted with water to fifty times its volume, hydrochloric acid and soluble chlorides no longer produce a precipitate; if still more and more diluted the sulphates, iodides, and chromates in turn fail to give evidence of the presence of lead, and, finally, a solution may be obtained so dilute that even hydrogen sulphide produces no visible effect. This difference in the relative "delicacy" of the various "tests for lead" evidently depends very largely on the difference in solubility of the precipitates in water—although it must not be forgotten that their color also has something to do with it, and that a minute quantity of the *black* sulphide is more easily seen when suspended in a large quantity of water, than is an equal quantity of the white phosphate, for instance, under the same circumstances—and experiments of the kind just referred to, when

carried out with solutions of known composition, furnish a
ready means of approximately determining the relative
solubility of the various "insoluble" salts.

That a certain test is "delicate" is, however, no proof
that it is "characteristic." The reaction with hydrogen
sulphide is by far the most delicate of the tests for lead, but
as a great nnmber of the other metals form black insoluble
sulphides, it is one of the least "characteristic," standing in
this respect far behind the precipitation as chloride.

The Solution of Precipitates.

(a) In Salt Solutions.—If a solution of sodium nitrate be
poured on lead sulphate, as the latter is far from being abso-
lutely insoluble, a certain small quantity of it will dissolve, and
once dissolved will react with the sodium nitrate to form lead
nitrate and sodium sulphate, according to the equation

$$2NaNO_3 + PbSO_4 \rightleftharpoons Na_2SO_4 + Pb(NO_3)_2$$
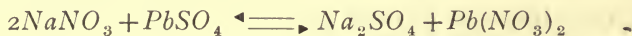
To replace the lead sulphate thus decomposed, a new portion
will dissolve, and this process of solution and decomposition
will go on until the lead nitrate and sodium sulphate formed
can maintain equilibrium with the remaining sodium nitrate,
and as much lead sulphate as will saturate the solution.
From a consideration of this case it is clear that, speaking
generally, insoluble salts will dissolve to a greater extent in
solutions of the salts of another acid than in pure water. But
even if a very concentrated solution of sodium nitrate were
able to dissolve one hundred times as much lead sulphate
as the same volume of pure water, it does not follow at all
that this increase in solubility would be detected by the rough
means at the disposal of the qualitative analyst. The chloride
of lead is at least one hundred times as soluble as the sulphate,
and yet passes for an "insoluble" salt. If, however, lead sul-
phocyanide had been substituted for the lead sulphate in the
preceding experiment, and if one hundred times as much of
it dissolved in the sodium nitrate solution as in water, the
actual quantity dissolved would be so much increased that the
difference would be noticeable even in test tube experiments,

and it would be said that "lead sulphocyanide is soluble in sodium nitrate solution." And if lead sulphocyanide, then *a fortiori* lead chloride; in short, the relative position in the series of solubility in sodium nitrate is the same as that in water, but the actual value in every case greater; hence in the former case the limit of "insolubility" appears nearer the sulphide end of the series. (See table.)

In the reactions just studied, for instance,

$$2NaNO_3 + PbSO_4 \rightleftharpoons Na_2SO_4 + Pb(NO_3)_2,$$
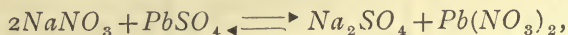
the only reason why more lead nitrate than lead sulphate exists in the solution at equilibrium is that a concentrated solution of sodium nitrate has been employed. If, however, there be substituted for the sodium nitrate a salt such as sodium chloride, which is capable of forming a double salt with the chloride of lead, a second force comes into play; and the lead chloride formed according to the equation

$$2NaCl + PbSO_4 \rightleftharpoons Na_2SO_4 + PbCl_2$$
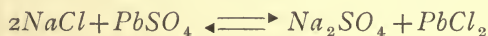
(which would about equal in quantity the lead nitrate of the preceding example) serves only as material for the formation of the double salt mentioned,

$$PbCl_2 + NaCl \rightleftharpoons PbNaCl_3.$$
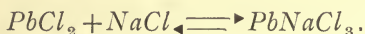
The consumption of lead chloride in this last reaction disturbs the equilibrium represented in the previous equation, and necessitates the solution of a fresh quantity of the "insoluble" salt.

From the examples here discussed it follows that :

(i.) The boundary line between "insoluble" and "soluble" lead salts will approach nearer the sulphide if, instead of water, a solution of sodium nitrate be used, and nearer still if the salt in solution can form a double salt containing lead.

(ii.) If in different cases different double salts be formed, that one will have the most effect on the solubilities which stands nearest the ferrocyanides in a series such as that suggested on page 20.
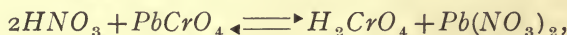
4

Solubilities of the "Insoluble" Lead Salts.

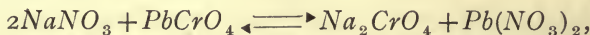| Name.	1,000 water.	10,000 water.	Sod. nitrate.	Sod. chloride.	Pot. bromide.	Pot. citrate.	Rochelle salt.	Sod. thiosulph.	Pot. iodide.	Amm. chloride.	100,000 water.	Potash.
Chloride............	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.
Thiosulphate........	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.
Sulphocyanide.......	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.
Ferrocyanide, etc.....	i.	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.	s.
Iodide	i.	*	i.	s.	s.	s.	s.	s.	s.	s.	s.	s.
Sulphate	i.	i.	i.	s.	s.	s.	s.	s.	s.	s.	s.	s.
Oxalate	i.	i.	i.	i.	i.	i.	s.	s.	s.	s.	s.	s.
Chromate	i.	i.	i.	i.	i.	i.	i.	i.	s.	s.	s.	s.
Phosphate	i.	i.	i.	i.	i.	i.	i.	i.	i.	i.	i.	s.
Sulphide	i.	i.	i.	i.	i.	i.	i.	i.	i.	i.	i.	i.

*Oxyiodide.

The letters *s* and *i* denote "soluble" and "insoluble" respectively in conc. solutions of the substances named at the head of the columns; in the columns headed "1,000 water," etc., the salts marked *i* may be obtained as ppts. (recognizable in a test-tube) from solutions containing one part of lead in 1,000, etc., of water. The hydrate and carbonate of lead have been omitted because of the formation of basic salts.

(b) *In acids or bases.*—If nitric acid, instead of a solution of sodium nitrate, be poured on a precipitate of chromate of lead, the difference between the equilibrium which ensues,

$$2HNO_3 + PbCrO_4 \rightleftarrows H_2CrO_4 + Pb(NO_3)_2,$$

and the other,

$$2NaNO_3 + PbCrO_4 \rightleftarrows Na_2CrO_4 + Pb(NO_3)_2,$$

may be seen from the following considerations: In the latter case, if solutions of the substances on the left hand of the $\rightleftarrows$ sign be mixed in equivalent quantities, just about one-half of the lead chromate will be converted into nitrate;

whereas in the former, owing to the great disparity in "strength" between the two acids (nitric and chromic), the lead will be converted almost entirely into the nitrate ; and if the two solutions be now each separately shaken up with lead chromate, a great deal more of that salt must dissolve in the former case than in the latter, before the concentration of the lead nitrate, etc., formed, is great enough to establish equilibrium in a solution saturated with the chromate.

This case, consequently, differs from the two others considered in this very important particular, viz.: it is not alone the solubility of the "insoluble" salt, but also the strength of its acid, that determines the amount dissolved at equilibrium. "If lead chromate will dissolve in potassium nitrate or in sodium chloride," it was argued before, "then lead sulphate, being more soluble in water, will dissolve still more readily in those solutions." In the case just considered this conclusion will not hold ; the greater strength of the sulphuric acid more than counterbalances the greater solubility of the lead sulphate, and the sulphate of lead is very little soluble in nitric acid, just as the phosphate, oxalate, and chromate, etc., are insoluble in the weak acetic acid.

If the acid of the insoluble salt be easily volatile at the temperature of the experiment, or if it readily decompose, giving rise to a volatile decomposition product, these will be important factors in determining the course of the reaction— *e.g.*, solution of carbonates, nitrites, sulphites, thiosulphates, etc., in acids ; similarly the greater volatility of sulphuric, nitric, and hydrochloric acids, at high temperatures, enables the non-volatile phosphoric and boracic acids to expel the former from their salts in the blowpipe reactions.

Other examples under this head are : the solution of the basic hydrates in acids, and that of the insoluble lead salts in potash.

The solutions of precipitates in acids or salt solutions (excluding the case where the acid of the insoluble salt is volatile) have some interesting properties. The solution formed by digesting lead sulphate with nitric acid until no more will dissolve, and filtering, gives a precipitate with sul-

phuric acid on the one hand, and with a concentrated solution of nitrate of lead on the other; in both cases the equilibrium

$$2HNO_3 + PbSO_4 \rightleftharpoons H_2SO_4 + Pb(NO_3)_2$$
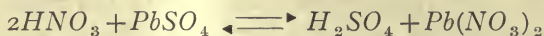
being disturbed in such a manner as to result in the formation of more lead sulphate. A consequence of this behavior is that if a little lead nitrate solution be mixed with a comparatively large quantity of concentrated nitric acid, and then dilute sulphuric acid added drop by drop, no precipitate will be produced by the first drops, and it is not until the quantity of sulphuric acid added is greatly in excess of that able to combine with the lead dissolved that the latter is even approximately separated in the form of sulphate.

The addition of water to the saturated solution of lead sulphate in nitric acid produces no precipitate, for though it decreases the concentration of the nitric acid it decreases equally that of the other three substances involved. Quite the contrary is the case when the solution contains a double salt ; in this case, for *one* substance whose concentration is diminished on one side of the equation *two* suffer dilution on the other, the equilibrium is disturbed, and a reaction takes place, resulting in the formation of these two. If, as is the case, in the equilibrium,

$$NaCl + PbCl_2 \rightleftharpoons NaPbCl_3,$$

one of the components, *e.g.*, $PbCl_2$, be insoluble, the water added may prove insufficient to retain in solution the new quantity of this substance formed, and in such a case (which frequently occurs) addition of water will produce a precipitate.

REACTIONS INVOLVING TWO OR MORE INSOLUBLE SALTS.

(*a*) *Two insoluble salts.*—If a fairly concentrated solution of potassium chromate be poured on a small quantity of lead carbonate* the conditions for the first moment are precisely the same as in the case discussed on page 50 (where lead

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*The formula of lead carbonate is written $PbCO_3$ for simplicity, the precipitate formed by sodium carbonate in lead salt solutions is really a basic carbonate.

chromate was the insoluble and sodium nitrate the dissolved salt). But long before the equilibrium

$$K_2CrO_4 + PbCO_3 \rightleftharpoons K_2CO_3 + PbCrO_4$$
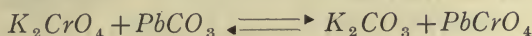
can be attained, the solution is saturated with chromate of lead, and the further progress of the reaction results only in the separation of this salt in the solid form, and the continual solution of fresh quantities of lead carbonate, until all of the latter has disappeared. Then, for the first time, it is possible for the concentration of the latter to fall below the limit fixed by its solubility, and the reaction comes to a standstill when the concentration of the lead carbonate dissolved, taken in connection with that of the remaining potassium chromate, is low enough to enable the resulting potassium carbonate and the quantity of lead chromate that can dissolve to balance the equilibrium.

The result may be expressed in words by saying that the potassium chromate has "transposed" the lead carbonate— the white precipitate of the carbonate has been replaced by a yellow precipitate of the chromate of lead.

A complete "transposition" of the carbonate is, however, not always the result of the reaction of potassium chromate on that salt. As long as the two "insoluble" salts are both present in the solid form, their concentrations in the solution depend, practically speaking, only on their solubilities and on the temperature, and is fixed by the conditions of the experiment; with the chromate and carbonate of potassium, on the other hand, the case is quite different; during the progress of the reaction the concentration of the former is continually growing less, and that of the latter greater; so that if a large quantity of lead carbonate be present to begin with, or if the solution of potassium chromate employed be dilute, the series of reactions just considered may come to an equilibrium before all the lead carbonate has disappeared—"partial transposition"; —while the effect of largely increasing the concentration of the potassium carbonate (by addition of that salt) is to reverse the reaction and from the chromate to regain the carbonate of lead—"reverse transposition."

In order that a transposition may be "reversible" the two

"insoluble" salts must not differ too much in their solubilities. The only way to compensate for the greater insolubility of the lead chromate in the case just considered is to employ a very concentrated solution of potassium (or sodium) carbonate; and a limit is set to this by the limited solubility of the alkali carbonates in water.   Thus, though ammonium sulphide transposes lead carbonate instantly with formation of the black sulphide, no solution of carbonates that it is possible to prepare is concentrated enough to effect the reverse change.

     An important corollary to what precedes is the conclusion that, if lead nitrate be added to a mixture of ammonium sulphide and sodium carbonate, all in solution, the precipitate will consist of lead sulphide only, until all the ammonium sulphide is used up. Similarly, when silver nitrate is added to a mixture of sodium chloride and potassium chromate, the red precipitate of silver chromate is not formed until all the chlorine has been removed from the solution.

     Here, as elsewhere, if acids be made use of as "reagents" in place of salt solutions, the distinction between "strong" and "weak" must not be lost sight of. Although sodium chloride cannot transpose lead chromate at all, and sodium sulphate only partially, the corresponding acids (hydrochloric and sulphuric) effect the change at once. In view of the similar cases already discussed, a detailed explanation of the reactions will be omitted.

     (b) *Four insoluble salts.*—Reactions involving more than two insoluble salts are not often met with in the course of analysis. One instance, however, may be mentioned here. When the two "insoluble" salts, lead chloride and silver chromate, are mixed under water a change of color (red to yellow) indicates that chromate of lead has been formed, and it will readily be seen that equilibrium in the reaction

$$PbCl_2 + Ag_2CrO_4 \rightleftharpoons PbCrO_4 + 2AgCl$$
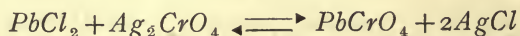
can be reached only when one or other of the salts on the left hand side of the equation has been completely dissolved. And it is equally clear that there is no means of reversing this result, unless, perhaps, *at some different temperature* the relative solubilities of the salts involved should be reversed.

The " Electro-Chemical Series."

A special case of the reaction involving two insoluble substances is that in which both of these are metals : *e.g.*, in the formation of the lead tree by tin in lead acetate solution, or of the silver tree by zinc in silver nitrate, also the deposition of mercury on a strip of copper in solutions of mercury salts, or of copper on a knife blade in cupric sulphate solutions.

$$Zn + CnSO_4 = Cu + ZnSO_4$$

Reactions of this nature are of especial interest, as they are made use of in the voltaic cell to generate an electric current, and the great majority of them can be reversed by electrical means. Equilibrium in these reactions depends not only on electrical forces, but also on the concentration of the salt solutions employed ; it takes a less electro-motive force to reverse the reaction formulated above (*i.e.*, to precipitate zinc from its salts by copper) if the zinc salts be concentrated and the copper salt dilute than in the opposite case ; in general, however, it is not possible to reverse the reaction by alteration in the concentrations alone.

As long as one of the ordinary ["strong"] salts be used, it does not matter which, the direction of the reaction remains the same, and it is possible to arrange the metals in a series— the electro-chemical series—such that each metal is precipitated from its salts by all those preceding it ; if, however, salts

Mg, Al, Zn, Cd, Fe, Ni, Pb, Sn, Cu, Sb, Bi, Ag, Hg, Pd, Pt, Au

such as mercuric cyanide* be employed, or if double salts be involved which have a great "tendency to be formed," the position of the metals in this series may be altered ; in solutions of potassium cyanide, for instance (which form such double salts with many of the metals), the arrangement in the electro-chemical series is as follows :

Zn, Cu, Cd, Sn, Ag, Ni, Sb, Pb, Hg, Pd, Bi, Fe, Pt.

*Introduction, page 19.

THE SECOND GROUP.

Commoner elements—(*Pb*), *Hg″, Cu, Bi, Cd, As, Sb, Sn.*
*Rarer elements*—*Au, Pt, Pd, Ru, Ir, Rh, Os, Te, Se, W, Mo.*

Metals whose sulphides are insoluble in dilute, 2—3%, hydrochloric acid, and whose chlorides are soluble in water.

The members of this group are precipitated as sulphides by hydrogen sulphide from the filtrate from Group I. The precipitate is often slimy, and tends to stop up the pores of the filter paper ; boiling for a few minutes with water and filtering hot is the best remedy.

Although the solution into which the hydrogen sulphide is led must contain free hydrochloric acid, in order to bring about the precipitation of arsenic and to prevent that of members of the third group, it must not be *too* acid, many of the sulphides of the second group being soluble in strong hydrochloric acid. This is specially noticeable in the case of tin and antimony ; one of the methods actually employed for the preparation of pure hydrogen sulphide being to act on antimonious sulphide with concentrated hydrochloric acid : in other words, the equation

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl,$$
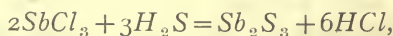
which represents the reaction in a slightly acid solution, must be reversed to represent that which takes place when the sulphide is treated with concentrated acid.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$
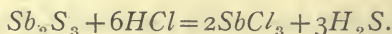
Consequently, in order to ensure the complete conversion into their sulphides of the metals of the second group, hydrogen

sulphide must be passed in until a portion of the filtrate *after dilution with water* gives no further precipitate with the gas.

Mixed with the sulphide in the second group precipitate is often found a quantity of free sulphur, arising from the oxidation of a portion of the hydrogen sulphide. This indicates the presence of oxidizing agents—nitric, chromic, or arsenic acids, ferric chloride, etc., etc.—in the solution, and may in great part be prevented by boiling the filtrate from Group I. with a few drops of alcohol ; if free nitric acid is known to be present, the solution should be evaporated nearly to dryness and water added before leading in the hydrogen sulphide.

## Group II. A. *As.Sb.Sn.*

The members of this group resemble one another in that their sulphides, with solutions of the sulphides of the alkali metals (and ammonium), form sulpho-salts—analogous to the oxy-salts produced by the action of their oxides (or hydrates) with solutions of the oxides (hydrates) of the alkalies. Compare, for example, the reaction

$$Sb_2S_3 + 6NH_4SH = 2(NH_4)_3SbS_3 + 3H_2S$$

with

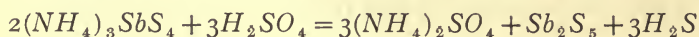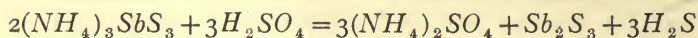$$Sb_2O_3 + 6NH_4OH = 2(NH_4'')_3SbO_3 + 3H_2O$$
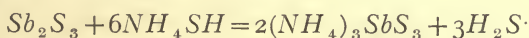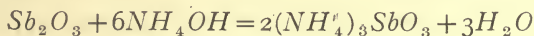
In analogy with the corresponding oxygen compound, the substance $(NH_4)_3SbS_3$ may be termed *ammonium ortho-sulph-antimonite*. The yellow ammonium sulphide used in the laboratory contains more sulphur than corresponds to the formula $(NH)_4SH$, (it may be considered as the solution of a mixture of various "polysulphides" of ammonium, such as $(NH_4)_2S_2$ $(NH_4)_2S_3$ etc.), and this extra sulphur acts on the sulph-antimonite, converting it into a sulph-antimoniate, exactly as oxygen would convert an antimonite into the corresponding antimoniate :—

$$(NH_4)_3SbS_3 + S_* = (NH_4)_3SbS_4$$
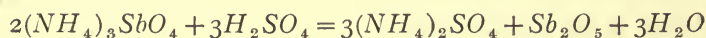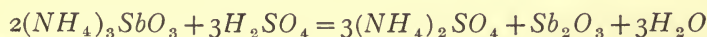$$(NH_4)_3SbO_3 + O_* = (NH_4)_3SbO_4$$
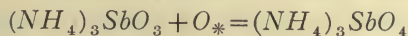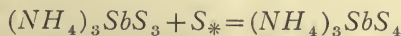
so that the solution obtained by digesting antimonious sulphide with *yellow* ammonium sulphide contains *ammonium ortho-sulphantimoniate.*
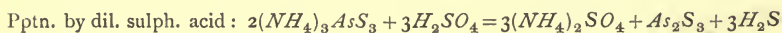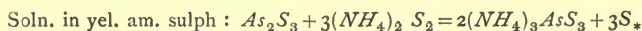
If now to a solution of an alkaline sulphantimonite or sulphantimoniate there be added an acid, *e.g.*, sulphuric acid, a salt (sulphate) of the alkali will be formed and one of the sulphides of antimony precipitated, with the liberation of hydrogen sulphide.
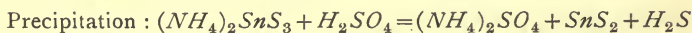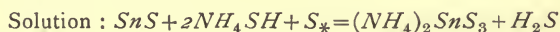
$$2(NH_4)_3SbS_3 + 3H_2SO_4 = 3(NH_4)_2SO_4 + Sb_2S_3 + 3H_2S$$

$$2(NH_4)_3SbS_4 + 3H_2SO_4 = 3(NH_4)_2SO_4 + Sb_2S_5 + 3H_2S$$

reactions analogous to the decomposition of the alkaline antimonites and antimoniates by acids :—

$$2(NH_4)_3SbO_3 + 3H_2SO_4 = 3(NH_4)_2SO_4 + Sb_2O_3 + 3H_2O$$

$$2(NH_4)_3SbO_4 + 3H_2SO_4 = 3(NH_4)_2SO_4 + Sb_2O_5 + 3H_2O$$

In the case of arsenious sulphide the reactions are :

Soln. in yel. am. sulph : $As_2S_3 + 3(NH_4)_2 S_2 = 2(NH_4)_3AsS_3 + 3S_*$

Pptn. by dil. sulph. acid : $2(NH_4)_3AsS_3 + 3H_2SO_4 = 3(NH_4)_2SO_4 + As_2S_3 + 3H_2S$

for the stannous sulphide :

Solution : $SnS + 2NH_4SH + S_* = (NH_4)_2SnS_3 + H_2S$

Precipitation : $(NH_4)_2SnS_3 + H_2SO_4 = (NH_4)_2SO_4 + SnS_2 + H_2S$

The sulphides of this group are also soluble in solution of potassium hydrate (and some of them in ammonia, sodium carbonate, ammonium carbonate, etc.), forming a mixture of sulpho and oxy-salts, from which, by the addition of acids, there is reprecipitated the same sulphide that was dissolved. For example :

$$As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsS_3 + 3CO_2 + (NH_4)_3AsO_3$$

$$(NH_4)_3AsS_3 + (NH_4)_3AsO_3 + 3H_2SO_4 = 3(NH_4)_2SO_4 + As_2S_3 + 3H_2O$$
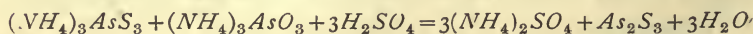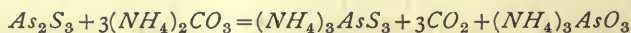
ARSENIC. $As = 74.52$.

OCCURRENCE.—*Ores :* realgar, As_2S_2 ; orpiment, As_2S_3 ; and mispickel, or arsenical pyrites, *FeAsS. Metallurgy :* the sulphide is roasted with iron, whereby the arsenic is set free and passes off in the form of vapor. *In commerce :* white arsenic, As_2O_3 ; fly powder, suboxide ; Paris green and Scheele's green (arsenites of copper).

ATOMIC WEIGHT.—*Stoech. fig.*: 22.173 grm. arsenic trichloride converted 39.597 grm. metallic silver into silver chloride. *Specific heat,* 0.0830. *Volatile compounds :* the metal ; arsine ; arsenic trioxide, As_2O_3 and As_4O_6; arsenic trichloride, bromide, etc.; and certain organic compounds. *Isomorphous relations :* with antimony and bismuth in the free state, and in Me_2S_3 ;   with   antimony   in Me_2O_3, $3Ag_2S.Me_2S_3$ and Cu_3MeS_4 ; with phosphorus in K_3MeO_4 and in the apatite group.

CHEMICAL RELATIONS.—In its molecular weight (As_4), in the formulæ and crystalline forms of its compounds, and in the existence of a gaseous hydride, arsenic closely resembles phosphorus and antimony, its next neighbors in the fifth column of Mendelejeff's table.   Like other members of the same column—bismuth excepted—the hydrates of its two oxides, As_2O_3 and As_2O_5, have acid properties ; and the chloride $AsCl_3$ ($AsCl_5$ unknown), though soluble in a small quantity of water, or in the presence of hydrochloric acid, is decomposed by much water with formation of arsenious and hydrochloric acids.   The sulpho·acids of arsenic are referred to on page 58.

THE COMPOUNDS OF ARSENIC.

Arsenic is a steel-grey brittle metal, *sp. gr.* 4.71, *volatile* at 450° C. ;   not oxidized in dry air, but gradually coated with arsenious anhydride As_2O_3 in moist air at ordinary temperatures ;   heated, it burns to form arsenious oxide. Arsenic   dissolves   readily   in   nitric   or   nitro-hydrochloric

acid, slowly in conc. sulph. acid (forming arsenic acid), not in hydrochloric acid ; soluble in solution of potash.

NAME.	Color.	Solubility in 100 parts water.		Remarks.
		cold	hot	
ARSENIOUS.				
Bromide .... $As\,Br_3$	white	dec.	dec.	*m.p.* 20°C., *b.p.* 220°C.
Chloride .... $As\,Cl_3$	white	sol.	dec.	*m.p.* 18°C., *b.p.* 134°C.
Hydride .... $As\,H_3$	gas	5vols(0°1)	insol.	See page 68.
Iodide .... $As\,I_3$	brick red	s. sol.	dec.	Sublimes.
Oxide .... As_2O_3	white	4	9.5	Sol. dil. hydrochl. acid.
Sulphide .... As_2S_3	yellow	insol.	insol.	Sol. amm. sulph. and in [alk. carb.
ARSENIC				
Hydrate $H_3AsO_4\frac{1}{2}H_2O$	white	16.7	50	
Oxide .... As_2O_5	white	150	very sol.	
Sulphide .... As_2S_5	yellow	insol.	insol.	Other sulph: realgar As_2S_2

Arsenious compounds AsX_3, colorless in solution.

Arsenious sulphide, As_2S_3 ; hydrogen sulphide, (or sodium thiosulphate on boiling) in solutions of arsenious acid, acidulated with dilute hydrochloric acid, precipitates arsenious sulphide. In the absence of hydrochloric acid no precipitate is formed, but the solution is colored yellow.

Arsenic compounds AsX_5, colorless in solution.

Arsenic sulphide, As_2S_5 ; precipitated from boiling hydrochloric acid solution of arsenic acid by hydrogen sulphide. At ordinary temperatures, sulphur, arising from the reduction of arsenic to arsenious acid, is at first precipitated ; when this reduction is complete, arsenious sulphide is precipitated.

Arsenites (derivatives of H_3AsO_3, etc.), obtained by dissolving metallic arsenic, arsenious anhydride, or other arsenious compounds, in potash. A solution of an arsenite, *e.g.*, arsenious acid neutralized with a few drops of ammonia, gives the following characteristic reactions :

(i.) *Ferric hydrate* precipitates all the arsenic, as basic ferric arsenite—(antidote for arsenic !).

(ii.) *Silver nitrate* produces a yellow precipitate of silver arsenite, Ag_3AsO_3 ; soluble in ammonia and in nitric acid.

(iii.) *Cupric sulphate* yields no precipitate; on careful addition of potash, however, a green precipitate, $CuHAsO_3$

(Scheele's green), is formed ; addition of ammonia instead of potash produces Paris green NH_4CuAsO_3.

(iv.) *Stannous chloride*, in hydrochloric acid solution, precipitates amorphous arsenic, mixed with tin (brown black).

Arseniates (derived from H_3AsO_4, etc.), obtained by the oxidation of arsenious acid and arsenites. A solution of arsenic acid, neutralized with a few drops of ammonia, gives the following reactions :

(i.) *Silver nitrate* produces a red-brown precipitate of silver arseniate, Ag_3AsO_4, soluble in nitric acid and in ammonia.

(ii.) *Ammonium molybdate and nitric acid*, on warming, (*cf.* phosphoric acid) yield a yellow precipitate of arseniomolybdate of ammonia, $(NH_4)_3AsO_4 + 12 M_0O_3$; soluble in ammonia, reprecipitated by nitric acid.

(iii.) *Ammonium chloride, ammonia,* and then *magnesium sulphate* precipitate white crystalline ammonium-magnesium-arseniate $(MgNH_4)AsO_4$.

OXIDATION AND REDUCTION.—Arsenious acid is oxidized to arsenic acid by bromine water, chromates, iodine, conc. nitric acid, permanganates, etc. $H_3AsO_3 + Cl_2 + H_2O = H_3AsO_4 + 2HCl$. Arsenic cpds. are reduced to arsenious by potassium iodide in hydrochl. acid solution, by sulphurous acid, hydrogen sulphide, sodium thiosulphate, ferrous chloride, stannous chloride, etc. Arsenic and arsenious acids are reduced to metallic arsenic by stannous chloride in hydrochl. acid solution, and by metallic copper, cadmium, zinc, etc.

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda or potass. cyan. ; all compounds of arsenic volatilize ; the presence of arsenic is recognized by an odor of garlic. In a bulb tube, with potassium cyanide, free arsenic condenses and collects at the mouth of the tube, forming a steel-colored mirror.

ANTIMONY. $Sb = 119.00$.

OCCURRENCE.—*Ores :* stibnite, Sb_2S_3; allemontite, As_3Sb_2; and valentinite, Sb_2O_3. *Metallurgy :* the metal is obtained

from the sulphide by heating with iron filings; in the preparation of tartar emetic the sulphide is first roasted to convert it into the oxide, and then dissolved in cream of tartar. *In commerce :* metal; alloys, *e.g.,* type metal, pewter, Babbit metal, etc.; tartar emetic $C_4H_4K(SbO)O_6$; and Naples yellow (basic plumbous antimoniate).

ATOMIC WEIGHT.—*Stoech. fig.:* 14.4802 grm. antimonious sulphide reduced with hydrogen yielded 10.3476 grm. metallic antimony. *Specific heat,* 0.052. *Volatile compounds:* antimonious chloride, bromide, and iodide, antimony trioxide, and certain organic compounds. *Isomorphous relations :* with arsenic in Me_2O_3, in Me_2S_3, in $3Ag_2SMe_2S_3$, in Cu_3MeS_4, with bismuth in Me_2S_3.

CHEMICAL RELATIONS.—Antimony occupies a place in the fifth column of Mendelejeff's table, and in forming a gaseous hydride SbH_3, acids derived from the two oxides Sb_2O_3 and Sb_2O_5, and in the isomorphous relations of many of its compounds it closely resembles nitrogen phosphorus and arsenic. It stands below them in the column, however, and in forming a normal sulphate, and nitrate, and many basic salts, shows analogy to the more metallic bismuth. Like arsenic, germanium, and tin, it forms soluble sulpho-salts with the alkalies (see page 57).

THE COMPOUNDS OF ANTIMONY.

NAME.	Color.	Solubility in 100 parts water cold	hot	Remarks.
ANTIMONIOUS.				
Bromide ....$Sb Br_3$	white	dec	dec.	*m.p.* 90°C; *b.p.* 280° *No* $SbBr_5$.
Chloride ... .$Sb Cl_3$	white	sol.	dec.	*m.p.,* 72°C; *b.p.* 230; also $SbCl_5$
Hydrate...... . $Sb(OH)_3$	white	insol.	insol.	Sol. in alkali hydrates.
Iodide ....$Sb I_3$	......	dec.	dec.	Trimorphous:red,green,and yel.
Nitrate .... .$Sb(NO_3)_3$	white	dec.	dec.	Basic salts with water.
Oxide ....Sb_2O_3	white	insol.	insol.	Other oxides SbO_2, Sb_2O_5.
Oxychloride ..... $Sb OCl$	white	insol.	insol.	Sol. dil. hydrochl. acid.
Sulphate......$Sb_2(SO_4)_3$	white	dec.	dec.	Basic salts with water.
Sulphide .. ....Sb_2S_3	orange	insol.	insol.	Also $Sb_2 S_5$.
Hydride..... .. $Sb H_3$	gas	4 vol(10°)	insol.	See page 68.

Antimony is a bluish-white, lustrous metal, *sp. gr.* 6.97, *m.p.* 432°C. At ordinary temperatures it oxidizes slowly in moist air; it burns with formation of antimonious oxide, Sb_2O_3. It dissolves slowly in hot hydrochl. or sulphuric acids; it is acted on by nitric acid with formation of oxides, and by nitro-hydrochloric with formation of oxides and chlorides.

Antimonious compounds SbX_3, colorless in solution; mostly insol. in water owing to formation of basic salts, soluble in acidulated water.

Antimonious sulphide Sb_2S_3, precipitated from not too strongly acidulated solutions of antimonious compounds by hydrogen sulphide, sodium sulphide, and sodium thiosulphate on boiling. In neutral solutions a coloration only is produced.

Antimonious acid and antimonites.—Potash, ammonia, or ammonium carbonate, precipitates from solutions of antimonious salts, in the absence of tartrates and citrates,—

Antimonious oxide Sb_2O_3, soluble in excess of the reagent to form potassium, (or ammonium), antimonite $KSbO_2$. Upon evaporation, or upon long standing, this solution decomposes with separation of antimonious oxide. Potassium permanganate, and potassium dichromate, in acid solution, are *reduced* (decolorized) by antimonious acid.

Metantimonic acid; $HSbO_3$; white, insol., obtained by treating metallic antimony with an excess of conc. nitric acid, and evaporating; soluble in potash.

Pyroantimonic acid, $H_4Sb_2O_7$.—Metantimonic acid dissolves in hydrochl. acid, forming a solution of antimony pentachloride, Sb_2Cl_5, from which addition of much water precipitates pyroantimonic acid.

OXIDATION AND REDUCTION.—Antimonious compounds are oxidized to antimonic by action of bromine water, nitric acid, chromates, permanganates, etc. Antimonic compounds are reduced to antimonious by the action of hydrogen iodide or of stannous chloride. Antimonic and antimonious compounds are reduced to metallic antimony by metallic zinc.

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda or potassium cyanide, all antimony compounds are reduced to a white brittle globule of metallic antimony. This rapidly oxidizes, producing white fumes, and leaving a white crystalline deposit on the charcoal.

T I N   *Sn.* = 116.78.

OCCURRENCE.—*Ores :* the only ore of tin is cassiterite, or tin stone, SnO_2. *Metallurgy :* the ore is first roasted to drive off sulphur arsenic and other impurities, then reduced with charcoal, and finally purified by distillation. *In commerce :* metal ; alloys, *e.g.*, solder, bronze, Britannia metal, etc. ; various compounds used in dyeing, *e.g.*, tin salt $SnCl_2 2H_2O$, preparing salts, $Na_2SnO_3 + 3H_2O$, and pink salt, $SnCl_4 + 2NH_4Cl$.

ATOMIC WEIGHT.—*Stoech. fig.*: 45.8323 grm. of tin oxidized by nitric acid yielded 58.2519 grm. tin dioxide. *Specific heat*, 0.055. *Volatile compounds :* stannous chloride ; stannic chloride, bromide, and iodide. *Isomorphous relations*, with titanium, silicium, and zirconium in MeO_2 ; with silicium, etc., in K_2MeF_6.

CHEMICAL RELATIONS.—In Mendelejeff's table tin stands between germanium and lead, and, like them, forms two series of compounds, stannous SnX_2, and stannic SnX_4. Stannous hydrate is soluble in potash, and also in strong acids, in this resembling the hydrate of lead ; it is, however, a much weaker base than the latter, all its salts being decomposed by water, with formation of basic compounds. Tin dioxide behaves as the anhydride of an acid, " stannic acid," H_2SnO_3, corresponding to plumbic acid, and more remotely to silicic and carbonic acids. The tetrachloride resembles those of the other members of the same column, in being a liquid with a low boiling point. Both it and the dichloride form crystalline compounds with water, but are decomposed by much water ; they are soluble in hydrochloric acid. Like germanium and the other members of Group II. A, it forms a series of sulpho-salts (see page 58).

The Compounds of Tin.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
STANNOUS.				
Bromide. ....Sn Br$_2$2H$_2$O	white	sol.	dec.	Dec. by much water.
Carbonate... ......(basic)	white	dec.	dec.	Carb. soda ppts. hydrate.
Chloride ......Sn Cl$_2$2H$_2$O	white	271	dec.	Dec. by much water.
Ferrocyan.. . . Sn$_2$Fe(CN)$_6$	w. (gela.)	insol.	insol.	
Ferricyan. . .Sn$_3$(Fe(CN)$_6$)$_2$	white	insol.	insol.	
Hydrate.... .....Sn(OH)$_2$	white	insol.	insol.	Sol. in alkalies.
Iodide..... ....Sn I$_2$2H$_2$O	red. yel.	dec.	dec.	Sol. in alkali iodides.
Nitrate...Sn(NO$_3$)$_2$.20H$_2$O	white	deliq.	deliq.	Dec. by much water.
Oxalate ....Sn C$_2$O$_4$	white	insol.	insol.	
Oxide...............Sn O	black	insol.	insol.	Other oxide, SnO_2.
Phosphate..........(basic)	white	insol.	insol.	
Sulphate..........Sn SO$_4$	white	sol.	sol.	Sol't'ns deposit basic salts
Sulphide.......... ... .Sn S	br'wn bl.	insol.	insol.	Other sulphide, SnS_2 yel.
STANNIC.				
Chloride .. ..Sn Cl$_4$	liquid	sol.	dec.	$Sn Cl_4$.$5H_2O$ cryst.
Hydrate.........H$_2$Sn O$_3$	white	s. sol.	s. sol.	Sol. in alkalies.
Nitrate....... .Sn(NO$_3$)$_4$	white	dec.	dec.	
Phosphate..........(basic)	white	insol.	insol.	
Sulphate. ..Sn(SO$_4$)$_2$2H$_2$O	white	dec.	dec.	

Sol. in tartrates : all insol. stannous compounds except the sulphide.

Tin is a lustrous, white metal, *sp.gr.* 7.30, *m.p.* 232°C.; tarnishes slowly in air ; burns at white heat to form stannic oxide SnO_2. Dissolves slowly in dil. hydrochl. and sulph. acids, rapidly if these acids be hot and concentrated, readily in dil. nitric acid, or in nitro-hydrochl. acid.

Stannous compounds, SnX_2, colorless in solution.

Stannous hydrate $Sn(OH)_2$.—The fixed alkalies, ammonia, alkali carbonates, barium carbonate, and potassium cyanide precipitate stannous hydrate ; soluble in excess of fixed alkali (*not* in ammonia or carbonates, distinction from antimony), forming stannites, *e.g.*, K_2SnO_2.

Stannic compounds, SnX_4, colorless in solution.

Stannic hydrate H_2SnO_3 (stannic acid).—The fixed alkalies, ammonia, alkali carbonates, sodium sulphate, and potassium iodide precipitate stannic hydroxide insol. in ammonia and ammonium carbonate, soluble in alkali carbonates, forming stannates.

5

Metastannic acid, $H_{10}Sn_5O_{15}$(?).*—The action of nitric acid on metallic tin is important.   Very dilute acid converts it into stannous nitrate, with simultaneous formation of ammonium nitrate ; conc. nitric acid, on the other hand, converts it into metastannic acid, which has the same composition as stannic acid, but differs from it, however, in the following respects: (i.) it is completely insol. in nitric acid; (ii.) boiled with conc. hydrochl. acid it is converted into metastannic chloride insol. in the conc. acid, but soluble in water, from which solution it is precipitated upon addition of sulph. acid ; (iii.) boiled with solution of caustic soda it forms sodium metastannate, insol. in excess, but soluble in water; (iiii.) by fusion with alkalies it is converted into salts of ordinary stannic acid ; on the other hand, stannous chloride boiled with hydrochl. acid, or even on standing, forms metastannic acid.

OXIDATION AND REDUCTION.—Stannous compounds are oxidized to stannic by nitric acid, sulphuric acid (hot), chlorine, bromine, iodine, mercuric chloride, etc. (Stannous chloride is a powerful reducing agent, reducing even nitrous acid, sulphurous acid, and potassium ferrocyanide.) Stannic compounds are reduced to stannous by metallic copper and tin.   Stannous and stannic compounds deposit metallic tin on aluminium, cadmium, magnesium, zinc, etc.

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda (more readily upon addition of potassium cyanide), all compounds of tin are reduced to a malleable metallic globule.   At the same time, a slight white *incrustation,* SnO_2, is formed on the charcoal, which, moistened with cobalt nitrate and ignited, becomes blue-green.

*Isomeric with stannic acid, molecular weight unknown.

SEPARATION IN GROUP II A.

In order to separate the members of Group II A from the Group II. precipitate, the latter, after being well washed, is treated with a *little* (2—4cc.) of the yellow ammonium sulphide solution, warm, but not boiling, according to either of the two methods described for the solution of lead chloride on page 45. A portion of the solution so obtained is filtered off and acidified with dilute sulphuric acid. If the precipitate consist merely of light yellow, milky, finely divided sulphur, burning without residue, nothing has dissolved in the ammonium sulphide, Group II A is absent; if, however, a curdy yellow to brown* precipitate be formed, the whole of the filtrate must be treated with excess of dilute sulphuric acid, and the precipitate analyzed for members of Group II A, while the residue from the ammonium sulphide solution must be thoroughly washed with successive small quantities of warm ammonium sulphide before testing for Group II B. These washings should be thrown away, and not used to dilute the Group II A solution.

ARSENIC may be separated from ANTIMONY and TIN either (*a*) by warming the sulphides As_2S_3, Sb_2S_5, SnS_2 with ammonium carbonate solution, which dissolves the sulphide of arsenic, leaving the other two; or (*b*) by warming them with concentrated hydrochloric acid, which leaves the arsenic and dissolves the others. Neither of these methods is very satisfactory, however; in the former a little antimony, and in the latter a little arsenic, goes into solution.

TIN may be separated from ARSENIC and ANTIMONY by dissolving the sulphides in warm dilute hydrochloric acid, with addition of a crystal of potassium chlorate, boiling the solution to expel free chlorine, adding sodium thiosulphate and boiling again; whereupon the arsenic and antimony are precipitated

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*The dark color is due to the presence of cupric sulphide, which is slightly soluble in yellow ammonium sulphide. Solutions of the polysulphides of potassium and sodium do not dissolve the sulphide of copper, but dissolve that of mercury.

as the sulphides As_2S_3 and Sb_2S_3, while the tin remains in solution. To bring about complete precipitation the sodium thiosulphate must be present in large excess, and the boiling must be continued some time. From the precipitate the arsenic may be removed by either of the methods given above.

The only really accurate separation, however, is that known as " MARSH'S TEST." Nascent hydrogen reduces compounds of tin to the metal, while those of arsenic and antimony are converted into the gaseous hydrides *Arsine* AsH_3, and *Stibine* SbH_3, respectively. The two gases may be distinguished by their action on silver nitrate solution, or by burning them and examining the products of their combustion. The methods of separation and identification based on these facts go by the name of " Marsh's Test," and may be carried out as follows :

(a) *Silver nitrate test.* — A flask of 200 *cc.* capacity, the " generator," is fitted by means of a perforated cork to a glass tube twice bent at right angles and dipping into a dilute solution of silver nitrate in a test-tube ; (a second tube, the " funnel tube," widened at the upper end and passing through the cork almost to the bottom of the flask, is very convenient for adding successive small portions of the liquid to be analyzed). Into the generator is put a little pure granulated zinc ; and the substance supposed to contain arsenic, antimony, or tin, dissolved in excess of dilute hydrochloric or sulphuric acid, is added. If arsenic or antimony be present, the gas evolved will produce a black precipitate of metallic silver or silver antimonide, respectively,

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$$
$$SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3$$
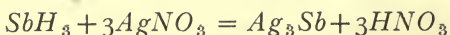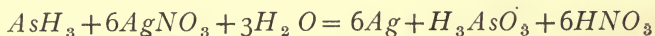
in the silver nitrate solution.* As, however, the precipitate might consist of silver sulphide (due to hydrogen sulphide from sulphur compounds in the generator), the presence of the two elements first mentioned must be proved by a further examination as follows : the black precipitate is re-

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* In concentrated (50%) solutions of silver nitrate, arsenic produces a yellow precipitate of Ag_3As, which is decomposed by water into arsenious acid and metallic silver.

moved from the solution by filtration, washed, warmed with dilute hydrochloric acid

$$Ag_3Sb + 6HCl = SbCl_3 + 3AgCl + 3H_2,$$

and the solution tested for antimony ; while the filtrate, after being freed from silver by the addition of dilute hydrochloric acid and filtering, is tested for arsenic. Any tin present will remain in the generator, the contents of which should be dissolved in dilute hydrochloric acid, and the solution tested for stannous salts by mercuric chloride, potassium permanganate, hydrogen sulphide, etc.

(b) *Combustion test.*—For this purpose the bent tube of the generator should be replaced by a short upright tube, drawn out at the upper end to a fine opening—the gas jet. Before igniting the escaping gas, a portion should be collected in a test-tube, inverted over the jet and conveyed with the orifice downward, and closed with the thumb, to the neighborhood of a flame ; if the gas take fire with a slight puff, and then burn quietly, the apparatus is free from air ; if, however, the contents of the test-tube ignite with a whistling noise, the air has not been completely driven out of the generator, and the application of a light to the jet would, in all probability, cause an explosion.   When the apparatus is finally freed from air, the gas should be ignited at the jet (if the generator be provided with a funnel tube, this is the time to add the solution), and a porcelain evaporating dish held in the flame.   If arsine or stibine be present, the gas will burn with a bluish-white flame (As_2O_3, Sb_2O_3), and black spots of metallic arsenic or antimony will be formed on the porcelain.

The *arsenic spots* are brown-black, and shining, soluble in alkaline solution of sodium hypochlorite, and turned yellow by warming with ammonium sulphide.   In dilute nitric acid they dissolve, and if silver nitrate, and then a little ammonia, be added to the drop of nitric acid solution, a yellow precipitate Ag_3AsO_3 is formed.

The *antimony spots*, on the other hand, are dull black, insoluble in the hypochlorite, and turned orange by ammonium sulphide.   Dilute nitric acid turns them white, Sb_2O_3, and, if to this white spot silver nitrate and then ammonia be added, it is blackened with formation of Ag_4O, more quickly on warming.

BISMUTH.　$Bi = 207.34$.

OCCURRENCE.—*Ores :* native; bismuth ochre, Bi_2O_3; and bismuth glance, Bi_2S_3. *Metallurgy :* metallic bismuth is obtained from its ores by roasting, and subsequent reduction with iron or charcoal. *In commerce :* metal; alloys, *e.g.*, Wood's metal, Rose's metal, etc.; and " magisterium bismuthii," $Bi(NO_3)_3$, $5H_2O$.

ATOMIC WEIGHT.—*Stoech. fig.:* (i.) 23.5866 grm. bismuth oxidized by nitric acid yielded 26.310 grm. bismuth oxide; (ii.) 16.6450 grm. bismuth oxide yielded 25.2551 grm. bismuth sulphate. *Specific heat,* 0.0288. *Isomorphous relations :* with arsenic and antimony, in the metal and in Me_2S_3.

CHEMICAL RELATIONS.—Bismuth, standing at the foot of the fifth column in Mendelejeff's classification, forms no hydride, but resembles the other members of the column in its derivatives of the types BiX_3 and BiX_5. Bismuthous hydrate is a weak base (*cf.* the hydrates of Group III A); its salts with the stronger acids are all decomposed by water (with formation of basic salts), while no salts with the weaker acids, *e.g.*, thiosulphuric, hydrocyanic, etc., are known; it does not, however, act as an acid toward potash. The hydrate of the pentoxide $HBiO_3$ (*cf.* HNO_3) is a very weak acid; its salts with the alkalies have been prepared by the action of bromine or chlorine on bismuthous hydrate suspended in potash or soda solution; halogen compounds of the type BiX_5 have not been prepared.

THE COMPOUNDS OF BISMUTH.

Bismuth is a reddish-white, brittle metal, often showing iridescence from superficial oxidation, *sp.gr* 9.9, *m.p.* 267°*C.*, *b.p.* 1300°*C.* At ordinary temperature not oxidized in air; burns to form bismuth oxide, Bi_2O_3; dissolves in cold nitric acid without evolution of hydrogen, in hot conc. sulph. acid with evolution of sulphur dioxide; insol. in dil. hydrochl. and sulphuric acids.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
BISMUTHOUS.				
Acetate $..Bi(C_2H_3O_2)_3$	white	sol.	sol.	
Bromide $........Bi\ Br_3$	yellow	deliq.	dec.	
Carbonate $.......$ (basic)	white	insol.	insol.	Dec. above $100°C.$
Chloride $.......\ Bi\ Cl_3$	white	dec.	dec.	Oxychlor. sol. dil. hydrochl.
Chromate $.......$ (basic)	yellow	insol.	insol.	Sol. dil. acids.　　[acid.
Ferrocyan $Bi_4(Fe(CN)_6)_3$	wh. yel.	insol.	insol.	Insol. in dil. acids.
Ferricyan. $Bi\ Fe(CN)_6$	br. yel.	insol.	insol.	Insol. in dil. acids.
Hydrate $.....Bi\ (OH)_3$	white	insol.	dec.	Forms oxide on heating.
Iodide $.....\ :....Bi\ I_3$	dark brown	sol.	dec.	S. ex.
Nitrate $Bi\ (NO_3)_3 5H_2O$	white	dec.	dec.	Basic salt sol. dil. nitric.
Oxalate $....Bi_2(C_2O_4)_3$	white	insol.	dec.	
Oxide $.....\ ....Bi_2O_3$	yellow	insol.	insol.	Other oxides $BiO,\ Bi_2O_4,$
Phosphate $.....Bi\ PO_4$	white	insol.	insol.	$[Bi_2O_5$
Sulphate $....Bi_2(SO_4)_3$	white	dec.	dec.	Basic salt sol. sulph. acid.
Sulphide $........Bi_2S_3$	black	insol.	insol.	

S. tartrates : chromate, ferricyan, ferrocyan, and hydrate.

Bismuthous compounds.—BiX_3, colorless in solution.

Bismuthous hydrate, $Bi\ (OH)_3$, precipitated from solutions of bismuthous salts by alkali hydrates and by potassium cyanide.

Bismuth monoxide, BiO, black, precipitated from solutions of bismuthous compounds by addition of potassium stannite* or by addition of solution of dextrose and heating.

Bismuthic acid, $HBiO_3$, red.　Obtained by addition of bromine water to a conc. solution of potash in which bismuthous oxide is suspended ; it decomposes readily on heating.

OXIDATION AND REDUCTION.—Bismuthous compounds to bismuthic by heating in the air, or by the action of chlorine or bromine in conc. potash solution.　Bismuthous salts are reduced to bismuth monoxide by potassium stannite, and by dextrose ; bismuthous compounds deposit metallic bismuth upon copper, cadmium, iron, lead, tin, zinc, etc.

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda, all compounds of bismuth are reduced to a brittle easily fusible globule, producing at the same time an *incrustation*, orange yellow, hot ; lemon yellow, cold.　*Borax and microcosmic salt beads :* in both flames, faintly yellow, hot ; colorless, cold.

*Prepared by the addition of potash to stannous chloride in sufficient excess to dissolve the precipitate, $Sn(OH)_2$, at first formed.

COPPER. $Cu = 63.12.$

OCCURRENCE.—*Ores :* native ; red copper ore Cu_2O ; mala-chite, $Cu(OH)_2CuCO_3$; copper glance, CuS; and copper pyrites $CuFeS_2$. *Metallurgy :* the metal is obtained from the oxide by reduction with charcoal ; the sulphide is first roasted to convert part of the sulphide into oxide, then upon raising the temperature the oxide formed reacts with the undecom-posed sulphide to set free copper, according to the equation $2\ CuO + CuS = 3Cu + SO_2$. *In commerce :* metal; alloys, *e.g.,* brass, bronze, German silver, etc. ; blue vitriol, $CuSO_45H_2O$; and Paris green, $CuHAsO_3$.

ATOMIC WEIGHT.—*Stoech. fig.:* (i.) 20.3270 grm. cupric oxide yielded 16.2279 grm. metallic copper. (ii.) Electrolytically, one grm. of copper is equivalent to 3.406 grm. of silver. *Specific heat,* 0.093. *Isomorphous relations :* with iron, nickel, cobalt, manganese, zinc, and magnesium, in $MeSO_47H_2O$; with these together with mercury and cadmium, in $MeSO\ .\ K_2SO_46H_2O.$*

CHEMICAL RELATIONS.—Copper forms two series of salts : the cuprous, CuX, white, mostly insoluble in water, are com-parable to the salts of silver, to the mercurous, aurous, and to the thallious salts ; while the cupric, CuX_2, are more like those of the magnesium group ; numerous insoluble basic cupric salts are known, the solutions of the normal salts react acid to litmus, and the hydrate loses water and is converted into the oxide below 100° C. Of the third series of derivatives of copper, corresponding to the oxide Cu_2O_3, little is known. Copper salts combine with ammonia. The metal itself is one of the best conductors of heat and electricity.

THE COMPOUNDS OF COPPER.

Copper is a soft, malleable, reddish metal; *sp. gr.* 8.94, *m. p.* 1054° C. In dry air at ordinary temperatures unchanged ; in moist air it becomes gradually coated with basic carbonate. It dissolves in acids without evolution of hydrogen : slowly in

*Ammonia may replace potassium in these double salts.

dilute hydrochloric and sulphuric acids, readily in dilute nitric acid, and with evolution of sulphur dioxide in hot concentrated sulphuric acid.

NAME.	Color.	Solubility in 100 parts		Remarks.
		cold	hot	
		water		
CUPRIC				
Acetate $Cu(C_2H_3O_2)_2 2H_2O$	blue	7 (20°)	20 (100°)	
Bromide.... $Cu\,Br_2 2H_2O$	black	deliq.	deliq.	Green basic bromides.
Carbonate..........(basic)	blue or grn.	s. sol.	s. sol.	Forms oxide on heating.
Chloride...... $Cu\,Cl_2 2H_2O$	green	60	very sol.	Conc. solutions green.
Chromate ....(basic)	br. yellow	s. sol.	s. sol.	
Cyanide......... $Cu\,(CN)_2$	br. yellow	insol.	insol.	S. ex. ; dec. on standing.
Ferrocyan... $Cu_2Fe(C_6N)_6$	red br.	insol.	insol.	Insol. in dil. acids.
Ferricyan... $Cu_3(Fe\,CN_6)_2$	yel. grey	insol.	insol.	Insol. in dil. *HCl*.
Hydrate........ $Cu\,(OH)_2$	pale blue	insol.	dec.	Forms oxide on heating.
Nitrate... $Cu\,(NO_3)_2 6H_2O$	blue	very sol.	very sol.	Forms oxide on heating.
Oxalate..,....... $Cu\,C_2O_4$	blue wh.	insol.	insol.	
Oxide......... .... $Cu\,O$	black	insol.	insol.	Heated evolves oxygen.
Phosphate ...... $Cu_3(PO_4)_2$	blue grn.	insol.	insol.	
Sulphate .... $Cu\,SO_4 5H_2O$	blue	40	203	
Sulphide...... ... $Cu\,S$	black	0.0001	insol.	S. sol. amm. sulphide.
Sulphocyan .... $Cu\,(SCN)_2$	black	insol.	insol.	Dec. on warming.
Thiosulph........ $Cu\,S_2O_3$	white	insol.	dec.	Dec. on warming.

Sol. in ammonia : all insol. cupric salts except sulphide.
Sol. in pot. cyan. : all insol. cupric salts.
Sol. in tartrates : all insol. cupric salts except the sulphide and ferrocyanide.
Sol. in ammon. chl. : cupric cyanide and carbonate.

Cuprous compounds.—CuX, colorless in solution (except where the acid is colored), insoluble in water ; easily soluble in concentrated ammonia, concentrated hydrochloric, hydrobromic, etc., acids; reprecipitated upon addition of water ; no sulphate or nitrate known.

Cuprous cyanide CuCN, white, insoluble. In solutions of *cupric* salts, potassium cyanide produces a red precipitate of cupric cyanide ; converted on boiling into cuprous cyanide with evolution of cyanogen gas, C_2N_2.

Cuprous hydrate CuOH, yellow, insoluble ; from alkaline solutions of *cupric* salts by solution of dextrose ; heated, red cuprous oxide　formed.

Cuprous iodide CuI, white, insoluble ; from solutions of *cupric* salts by potassium iodide ; (precipitate colored dark brown from separation of free iodine). This precipitation is

complete only in the presence of such reducing agents as
sodium thiosulphate, ferrous sulphate, etc.

Cuprous sulphocyanate, $CuSCN$, white, insoluble. Potassium
sulphocyanate in solutions of *cupric* salts precipitates cupric
sulphocyanate (black), converted into cuprous sulphocyanate
upon warming, or in presence of sulphur dioxide.

Cuprous thiosulphate, $Cu_2S_2O_3$, white, insoluble. Sodium
thiosulphate in concentrated solutions of *cupric* salts precipi-
tates cupric thiosulphate, yellow, which upon standing changes
slowly into cuprous thiosulphate, white, and finally into
cuprous sulphide, black.

Cupric compounds CuX_2, anhydrous, white; dilute solu-
tions, blue; concentrated solution of cupric chloride, green.
The dilute blue solution of this salt becomes green upon
addition of concentrated hydrochloric acid.

Salts of cupric acid (derived from Cu_2O_3 ?). Cupric
nitrate added to water holding bleaching powder in suspen-
sion produces a precipitate at first green, afterwards violet,
which, upon standing or washing, becomes converted into
blue cupric hydrate.

OXIDATION AND REDUCTION.—Cuprous compounds are
oxidized to cupric by the action of heat and by acids. Cupric
compounds are converted into cuprates by the action of
bleaching powder. Cupric compounds are reduced to
cuprous by the action of stannous chloride, arsenious acid, or
dextrose in alkaline solution, also by potassium iodide,
potassium cyan., and potassium sulphocyan. Cupric and
cuprous solutions deposit metallic copper upon aluminium,
cadmium, iron, lead, tin, zinc, etc. See p. 55.

BLOWPIPE REACTIONS.—*B. B. on C.*, with carb. soda, all
copper compounds are reduced to metallic copper. *Borax
bead : O.F.*, green, hot ; blue, cold ; *R.F.*, colorless, hot ; reddish
brown, cold. *Microcosmic salt bead : O.F.*, green, hot; blue, cold ;
R.F., green, hot ; reddish brown, cold. All copper compounds,
moistened with dil. hydrochloric acid, impart a green or
greenish blue color to the flame.

CADMIUM. $Cd = 111.18$.

OCCURRENCE.—*Ores :* greenockite, CdS ; to the extent of two or three per cent. in most zinc ores. *Metallurgy :* obtained as by-product in the manufacture of zinc. *In commerce :* metal ; alloys, *e.g.,* Wood's metal, cadmium amalgam ; cadmium iodide, CdI_2 (photography) ; and cadmium yellow, CdS.

ATOMIC WEIGHT.—*Stoech. fig.:* 64.2051 grm. cadmium sulphate yielded 44.4491 grm. cadmium sulphide. *Specific heat,* 0.0567. *Volatile compounds :* metallic cadmium, cadmium chloride, bromide, and iodide. *Isomorphous relations :* with copper, magnesium, zinc, mercury, iron, nickel, cobalt, and manganese in $MeSO_4, K_2SO_4, 6H_2O$.

CHEMICAL RELATIQNS.—In Mendelejeff's table cadmium stands in the second column, between zinc and mercury ; it resembles the former in its position in the electro-chemical series, in the appearance of the metal, and in the isomorphous relations of some of its salts.   It forms but one series of salts, whose solutions react acid to litmus ; the chloride is not decomposed by water, and no insoluble basic salts are known. Unlike zinc, it does not dissolve in potash. Cadmium iodide is a rather " weak " salt (see Introduction, page 19).

THE COMPOUNDS OF CADMIUM.

Cadmium is a white malleable metal, *sp. gr.* 8.67, *m.p.* 320. Not oxidized in air at ordinary temperatures ; burns in air to form cadmium oxide, CdO (brown).   Dissolves slowly in concentrated hydrochloric and sulphuric acids with evolution of hydrogen, readily in concentrated nitric acid with evolution of oxides of nitrogen.

All compounds of cadmium are colorless in solution ; except those whose acids are colored.

OXIDATION AND REDUCTION.—All compounds of cadmium deposit metallic cadmium upon zinc, magnesium, and aluminium.

NAME.	Color.	Solubility in 100 parts water.		Remarks.
		cold	hot	
$Acetate\ Cd(C_2H_3O_2)_2.6H_2O$	white	very sol.	very sol.	
$Bromide \ldots \ldots Cd\,Br_2 2H_2O$	white	deliq.	deliq.	
$Carbonate \ldots \ldots \ldots Cd\,CO_3$	white	insol.	insol.	No basic carbonate.
$Chloride \ldots \ldots Cd\,Cl_2.2H_2O$	white	140	150	
$Chromate \ldots \ldots \ldots Cd\,CrO_4$	yellow	very sol.	very sol.	S. ex.
$Cyanide \ldots \ldots \ldots Cd(CN)_2$	white	insol.	insol.	S. ex.
$Ferrocyan \ldots Cd_2Fe\,(CN)_6$	white	insol.	insol.	Sol. dil. hydrochl. acid.
$Ferricyan \ldots Cd_3(Fe\,(CN)_6)_2$	yellow	insol.	insol.	Sol. dil. hydrochl. acid.
$Hydrate \ldots \ldots \ldots Cd\,(OH)_2$	white	insol.	insol.	S. alkali hydrate ($cf.\ Zn$)
$Iodide \ldots \ldots Cd\,I_2.2H_2O$	white	93(20°)	133(100°)	
$Nitrate \ldots ..Cd\,(NO_3)_2.4H_2O$	white	deliq.	deliq.	
$Oxalate \ldots \ldots \ldots Cd\,C_2O_4$	white	0.007	0.01	sol. ammonium oxalate.
$Oxide \ldots \ldots \ldots \ldots Cd\,O$	brown	insol.	insol.	
$Phosphate \ldots \ldots Cd_3(PO_4)_2$	white	insol.	insol.	Sol dil. acids.
$Sulphate \ldots Cd\,SO_4.\frac{8}{3}H_2O$	white	60	very sol.	No comp'd $Cd\,SO_4.7aq.$
$Sulphide \ldots \ldots \ldots Cd\,S$	yellow	insol.	insol.	Sol. 15% hot sulph. acid.

Sol. in ammonia and in pot. cyan.: all insol. cadmium salts except sulphide.
Sol. in tartrates : all insol. cadmium salts except ferrocyan., phosphate, and sulphide.
Sol. ammon. chlor.: all insol. cadmium salts except ferrocyan., hydrate, and sulphide.

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda, all compounds of cadmium are reduced. The metal vaporizes, forming an *incrustation* brown in the oxidizing flame, volatile in the reducing flame. *Borax and microcosmic salt beads :* in both flames, yellow, hot ; colorless, cold.

SEPARATION IN GROUP II B.

To the precipitate of the sulphides of Group II B, washed, and, if necessary, freed from members of Group II A by the treatment described on page 67, add dilute nitric acid and warm.

Residue : Mercuric sulphide, black, soluble in aqua regia. Sulphur :—$(HNO_3 + H_2S = ?)$.

Solution : Nitrates of lead, bismuth, copper, and cadmium.

To a part of the solution in nitric acid add a little dilute sulphuric acid ; if no precipitite be formed, even after addition of alcohol shaking and standing for a minute, *Lead* is absent ; if a precipitate be formed, the reagent must be added to the whole of the nitric acid solution, and the precipitated lead sulphate removed by filtration.

Then add ammonia in excess
White precipitate : Bismuthous hydrate.
Blue solution : Copper (soluble cupric ammonium salts).

To detect the presence of Cadmium : If copper be absent, add to the ammoniacal solution (freed from the hydrate of bismuth by filtration) ammonium sulphide. A yellow precipitate indicates cadmium, CdS.

If copper be present, one of two methods may be adopted.

(*a*) To the blue solution from which any precipitate of bismuthous hydrate has been removed by filtration, add potassium cyanide until decolorized, then ammonium sulphide ; a yellow precipitate indicates cadmium (the black cupric sulphide is soluble in potassium cyanide solution).

(*b*) Precipitate the sulphides of copper and cadmium from the blue solution (using hydrogen sulphide or ammonium sulphide), filter and wash the precipitate and warm it with dilute sulphuric acid, which dissolves the sulphide of cadmium, leaving that of copper undissolved ; filter, and test the filtrate for cadmium.

For CONFIRMATORY TESTS, see the description of each metal.

THE THIRD GROUP.

Commoner elements.—Fe, Cr, Al, Ni, Co, Zn, Mn.
Rarer elements.—Ur, Be, Th, Zr, Ce, Ti, Y, V, etc.

The third group consists of those metals which are not precipitated by hydrogen sulphide in dilute hydrochloric acid solution, but which are precipitated—some as sulphides, others as hydrates—by ammonium sulphide from a solution containing ammonium chloride.

The more commonly occurring metals of this group fall naturally into two classes : *Group III A*, those precipitated as hydrates, viz., iron, chromium, aluminium; and *Group III B*, those precipitated as sulphides, viz., nickel, cobalt, manganese, zinc. To separate these, the Group III precipitate may be dissolved in hydrochloric acid, and the members of the first subdivision precipitated either by treatment with *barium carbonate* in the cold, or by boiling with *sodium acetate*. It is, however, much more convenient to precipitate the hydrates of class A directly by adding ammonium chloride and ammonia to the filtrate from the second group (any iron present being previously oxidized by nitric acid), thus avoiding altogether the use of ammonium sulphide solution in Group III A. The use of ammonium chloride prevents the precipitation of magnesia and of members of Groups IV and V by the ammonia. A certain amount of the chloride of ammonium is formed in any case, when ammonia is added to the filtrate from the second group (containing hydrochloric acid) ; but this, while preventing complete precipitation of magnesia, manganese, etc., might be insufficient in quantity to keep them altogether in solution ; and the addition of a further portion of ammonium chloride guards against the incon-

venience of obtaining these metals partly in Group III A, and partly in Groups IV and V, respectively.

GROUP III A.

Iron, chromium, and aluminium are precipitated as hydrates of the formula $M(OH)_3$. These three, however, are not the only metals to form hydrates of this type, others, for example, being cobalt, nickel, bismuth, and antimony. All of these hydrates are alike in being very weak bases—none of them can drive ammonia from solutions of its salts, and some of them even act as acids toward potash—a similarity that appears to depend rather on the formula of the hydrate than on the position of the metal in Mendelejeff's table, as in general, where an element forms more than one hydrate, that derived from the highest oxide is always the more acid or less basic.* As has been pointed out in the Introduction, this weakness of the bases entails striking consequences in the chemical behavior of the solutions of their salts; the chlorides are all decomposed by water, though soluble in hydrochloric acid, the sulphides and most of the soluble salts are decomposed by water, especially on boiling, forming either the hydrate or some basic compound, while no carbonates,† nitrites, sulphites, thiosulphates, etc., are known; the carbonates, thiosulphates, etc., of the alkalies bringing about a precipitation of the hydrates.

The triacid bases fall into two natural classes : (i.) Iron, chromium, aluminium, cobalt, and manganese ; forming alums and spinelles. (ii.) Bismuth and antimony ; connected by the isomerism of their oxides, sulphides and salts, with arsenic and phosphorus. The latter, by reason of the insolubility of their sulphides in dilute hydrochloric acid, fall in Group II ; the reason that the others, iron, chromium, and aluminium, come down in Group III A, while cobalt and manganese pass into the next sub-group, lies in the difference between

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* Compare, for example, the hydrates corresponding to the monoxide, sesquioxide, and trioxide of chromium, and those of the various oxides of iron, manganese, bismuth, etc.

†Bismuth forms a basic carbonate.

these elements with respect to the relative stability of their different classes of salts under the conditions imposed by the plan of analysis adopted. Thus, the second group reagent, hydrogen sulphide in acid solution, reduces all derivatives of the higher oxides of chromium, iron, cobalt, and manganese (*e.g.*, chromates, ferric salts, manganates and permanganates, cobaltic salts, etc.), to salts of the form $CrCl_3$, $FeCl_2$, $CoCl_2$, $MnCl_2$, respectively, and of these latter the iron compounds alone are oxidized (forming ferric salts, *e.g.*, $FeCl_3$) on boiling with dilute nitric acid.

GROUP III B.

The sulphides of this group differ from those of Group II in being insoluble in dilute hydrochloric acid. That this distinction is one of degree only, follows from what has been said in the introduction to Group II as to the action of concentrated hydrochloric acid on the sulphides of that group, and from the fact that the sulphides of nickel, cobalt, and zinc are partially precipitated by hydrogen sulphide from dilute neutral solutions of their chlorides, *i.e.*, are insoluble in the very dilute hydrochloric acid produced by the reaction,

$$ZnCl_2 + H_2S = ZnS + 2HCl.$$
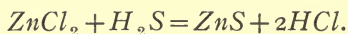
Acetic acid, being much " weaker " than hydrochloric acid, cannot dissolve any of the sulphides of the second group, and in the third group the sulphide of manganese is the only one dissolved in considerable quantity by it. As by the addition of sodium acetate to a zinc solution nearly all the hydrochloric acid of the last equation is converted into acetic acid and sodium chloride, it is possible to precipitate zinc, quantitatively, by hydrogen sulphide, from neutral or nearly neutral solutions, to which has been added an excess of sodium acetate, or of the sodium salt of any other weak acid forming a soluble salt with zinc.

The connection between the solubilities of the various sulphides in acids and in pure water may be seen from a consideration of the reaction :—

$$MCl_2 + H_2S \rightleftarrows MS + 2HCl.$$
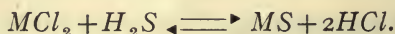
If the concentration of the H_2S and that of the HCl be the same in all cases, and assuming that none of the substances involved belong to the class of "weak" salts, the only reason why the concentration of the chlorides MCl_2 at equilibrium should vary from case to case must be that the concentration of the MS, *i.e.*, the solubility of the various sulphides, varies in a parallel manner. Thus, the solubilities in water of the sulphides of the second group are less than those of the third, and among the latter the sulphides of nickel and cobalt are the least soluble, next that of zinc, and, lastly, the sulphide of manganese. It must not be overlooked, however, that this conclusion depends on the assumption that none of the chlorides and sulphides involved belong to the class of the "weak" salts; and while it is *probable* that this holds for the sulphides in the extremely dilute solutions that they form with water, still nothing is known with certainty on this point.

ALUMINIUM. $Al = 26.90.$

OCCURRENCE.—*Ores :* corundum, ruby, sapphire (Al_2O_3); spinelle, $Mg (AlO_2)_2$; cryolite, $3NaF.AlF_3$; clay (hydrated silicate); in combination with other silicates in feldspar, mica, etc. *Metallurgy:* the metal is obtained by electrolysis of cryolite or by fusing this ore with sodium. *In commerce :* metal; alloys, *e.g.*, aluminium bronze; alum, $K_2Al_2(SO_4)_2$. $12H_2O$; ultramarine (aluminium sodium silicate with poly-sulphides of sodium); many other aluminium salts used in dyeing.

ATOMIC WEIGHT.—*Stoech. fig.:* 3.6745 grm. aluminium sulphate yielded 1.0965 grm. aluminium oxide. *Specific heat,* 0.214. *Volatile compounds :* aluminium chloride, bromide and iodide $(Al_2Cl_6$ at 440°C., $AlCl_3$ at 700°C.); organic compounds of aluminium. *Isomorphous relations :* with iron, chromium, and manganese, in* K_2SO_4 . $Al_2(SO_4)_3$. $24H_2O$, with iron and chromium, in the spinelles† $Mg(MeO_2)_2$, and in Me_2O_3.

*Potassium may be replaced by sodium, lithium, ammonium, rubidium, cæsium, and thallium.

†Magnesium may be replaced by manganese, zinc, and iron.

CHEMICAL RELATIONS.—Aluminium is one of the lightest of the metals. The hydrate is a weak base ; with acids it forms but one series of salts, of the type AlX_3, which resemble closely the corresponding derivatives of iron, chromium, manganese, and cobalt. With the stronger bases it takes the part of an acid, forming a series of *aluminates*, many of which occur as minerals. Like the other elements of low atomic weight, and non-metallic, or but slightly metallic, character, its atomic heat is considerably below 6.5.

THE COMPOUNDS OF ALUMINIUM.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
ALUMINIUM.				
Bromide .... $Al Br_3.6H_2O$	white	deliq.	deliq.	
Chloride. . ...$Al Cl_3.6H_2O$	white	400	very sol.	
Hydrate .... $Al (OH)_3$	white	insol.	insol.	Sol. dil. acids and alkal.
Iodide .... $Al I_3.6H_2O$	white	deliq.	deliq.	
Nitrate.......$Al(NO_3)_3.6H_2O$	white	deliq.	deliq.	
Oxide.............. .... Al_2O_3	white	insol.	insol.	
Phosphate ....$Al PO_4$	white	insol.	insol.	Sol. dil. acids.
Sulphate......$Al_2(SO_4)_3.18H_2O$	white	85	1130	
Sulphide ....Al_2S_3	yellow	dec.	dec.	Formed from elements.
Sulphocyan.......... $Al(SCN)_3$	white	very sol	very sol.	Known only in sol'n.
Pot. alum, ...	white	4 (0°)	357(100°)	
Sod. alum........,.............	white	47 (13°)	100(100°)	
Amm. alum..................	white	5 (0°)	422(100°)	

Sol. in tartrates : hydrate and phosphate.

Aluminium is a tin-white, malleable metal, *sp. gr.* 2.58, *m. p.* 700° *C.* If pure, not oxidized in air at ordinary temperatures. Dissolves slowly in dilute sulphuric acid, more readily in concentrated, rapidly in hydrochloric acid ; also soluble in the fixed alkalies.

Aluminium compounds AlX_3, colorless in solution.

Aluminium hydrate $Al(OH)_3$: fixed alkalies, ammonia, alkali carbonates, ammonium sulphide, sodium acetate, potassium cyanide, potassium ferrocyanide, and sodium thiosulphate precipitate aluminium hydroxide ; insoluble in ammonia and

ammonia salts, soluble in potassium or sodium hydrate, forming aluminates.

Potassium aluminate $KAlO_2$, white, soluble in water. In solution decomposed by all acids with separation of alumina Al_2O_3; also decomposed by ammonium salts on long standing in a warm place.

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda, all compounds of aluminium form the infusible oxide Al_2O_3; moistened with cobalt nitrate and reignited the oxide assumes a blue color (Thénard's blue).

IRON.　$Fe = 55.60$.

OCCURRENCE.—*Ores:* magnetic iron ore, Fe_3O_4; hæmatite, Fe_2O_3; spathic iron ore, $FeCO_3$; and iron pyrites, FeS (not used as a source of iron). *Metallurgy:* iron is obtained from its ores by first roasting it to convert into the oxide, and reducing the latter to the metallic state by heating with charcoal. *In commerce:* metal (iron and steel); green vitriol, $FeSO_4\ 7H_2O$; potassium ferrocyanide, $K_4Fe(CN)_6$; Prussian blue, $Fe_4(Fe(CN)_6)_3$.

ATOMIC WEIGHT.—*Stoech. fig.:* 12.5120 grm. ferric oxide on heating in a current of hydrogen yielded 8.7585 grm. metallic iron. *Specific heat,* 0.113. *Volatile compounds:* ferrous chloride, ferric chloride (Fe_2Cl_6 440°C, $FeCl_3$ 750°C). *Isomorphous relations:* with calcium, manganese, and magnesium, in $MeCO_3$; with magnesium, zinc, nickel, cobalt, and manganese, in $MeSO_4\ 7H_2O$; with aluminium, chromium, etc., in $K_2SO_4, Al_2(SO_4)_3, 24H_2O$; with copper, magnesium, zinc, cadmium, mercury, nickel, cobalt, and manganese, in $K_2SO_4, MeSO_4, 6H_2O$; with chromium and aluminium in spinelles, $Mg(MeO_2)_2$ and in Me_2O_3.

CHEMICAL RELATIONS.—Iron forms three series of compounds: the ferrous FeX_2, comparable to compounds of zinc, magnesium, etc.; the ferric FeX_3, resembling aluminium, chromic, etc., compounds; and the ferrates, *e.g.*, K_2FeO_4,

easily decomposed and little known, isomorphous with the chromates and sulphates. It is often said that of these three the ferric salts are the "most stable"; the student is warned against the use of indefinite expressions such as this. Ferrous salts, in solution, are partially converted into ferric salts by the action of the air—hence the reagent solution of ferrous sulphate almost invariably contains some ferric sulphate—so that, *under these circumstances*, the ferrous salts may truly be said to be "less stable" than the ferric. On the other hand, as ferric hydrate is a very "weak" base, dilute solutions of its salts are decomposed by boiling, with formation of insoluble basic ferric salts, [try a dilute solution of ferric chloride], and may, therefore, with equal truth be said to be "less stable"—under *these* circumstances—than the corresponding ferrous compounds, which are unaffected by boiling with water.

The Compounds of Iron.

Iron is a malleable metal attracted by the magnet, *sp. gr.* 8.0, *m. p.* 1275° C. to 1375° C. Soft iron wire contains 0.5 % carbon, steel 0.2 − 1.5 %, and cast-iron 2 − 5 %. In finely divided condition iron burns in air to form the oxide Fe_2O_3. It dissolves in nearly all acids with formation of corresponding salts. If pure, it is not acted upon by concentrated nitric acid.

Ferrous compounds, FeX_2, pale green in solution.

Ferrous sulphate.—A solution of this salt, free from ferric salts, may be obtained by treating iron tacks, wire, or filings with dilute sulphuric acid in a small, narrow-mouthed flask. As soon as the evolution of hydrogen becomes slow, the solution should be removed to a sand bath, and boiled, care being taken to have the iron in excess.

Ferric compounds, FeX_3, reddish brown in dilute solution.

Potassium ferrate, K_2FeO_4, obtained by fusing together iron filings and potassium nitrate. It is soluble in water, but the solution rapidly decomposes to form ferric hydrate, potash, and oxygen.

Potassium ferrocyanide, $K_4Fe(CN)_6$, obtained by dissolving ferrous cyanide $Fe(CN)_2$ in excess of potassium cyanide, or

by the action of potassium cyanide on metallic iron or its oxides. A solution of ferrocyanide of potash upon oxidation yields *potassium ferricyanide* $K_3Fe(CN)_6$. A solution of either of these salts gives none of the characteristic reactions of iron; heated with concentrated sulphuric acid, however, the double salts are decomposed and the corresponding sulphates are formed.

NAME.	Color.	Solubility in 100 parts water.		Remarks.
		cold	hot	
FERROUS.				
Acetate .....$Fe(C_2H_3O_2)_2$	white	very sol.	very sol.	
Bromide.... $Fe\,Br_2.6H_2O$	green	sol.	very sol.	
Carbonate ....$Fe\,CO_3$	grey white	insol.	insol.	Dec. in air to hydrate.
Chloride.....$Fe\,Cl_2.4H_2O$	white	130	very sol.	
Cyanide ....$Fe\,(CN)_2$	yel. red	insol.	insol.	S. ex. forms $K_4Fe(CN)_6$
Ferrocyan.....$Fe_2Fe(CN)_6$	light blue	insol.	insol.	Dark blue on standing.
Ferricyan ..$Fe_3(Fe(CN)_6)_2$	dark blue	insol.	insol.	Turnbull's blue n.s. acids
Hydrate..... ..$Fe\,(OH)_2$	grn. white	insol.	insol.	
Iodide ....$Fe\,I_2.5H_2O$	dark grn.	very sol.	dec.	
Nitrate..$Fe\,(NO_3)_2.6H_2O$	white	sol.	dec.	
Oxalate. ....$Fe\,C_2O_4$	white	0.02	0.03	Sol. in dil. acids.
Oxide ....$Fe\,O$	black	insol.	insol.	
Phosphate $Fe_3(PO_4)_2.8H_2O$	blue wh.	insol.	insol.	
Sulphate....$Fe\,SO_4.7H_2O$	green	60	333	Green vitriol.
Sulphide.............$Fe\,S$	black	insol.	s. sol.	Other sulphides : FeS_2.
Thiosulph ..$Fe\,S_2O_3.5H_2O$	green	very sol.	very sol.	
Amm. Sulphate....$(6H_2O)$	pale green	17	very sol.	
FERRIC.				
Acetate .....$Fe(C_2H_3O_2)_3$	dull red	very sol.	dec.	
Bromide ....$Fe\,Br_3$	red	s. sol.	sol.	
Chloride...... ....$Fe\,Cl_3$	garnet red	deliq.	deliq.	Low temp. Fe_2Cl_6.
Chromate ... . (basic)	brown	insol.	dec.	
Ferrocyan..$Fe_4(Fe(CN)_6)_3$	dark blue	insol.	insol.	Prussian blue, insol. dil.
Ferricyan....$Fe\,Fe\,(CN)_6$	brown	sol.	sol.	[acids.
Hydrate ....$Fe\,(OH)_3$	red brown	insol.	insol.	Insol. alkali hydrates.
Nitrate...$Fe(NO_3)_3.18H_2O$	white	very sol.	very sol.	
Oxalate ......$Fe_2(C_2O_4)_3$	white	insol.	insol.	Sol. oxalic acid.
Oxide . ... Fe_2O_3	grey	insol.	insol.	Other oxide Fe_3O_4.
Phosphate ...$Fe\,PO_4.4H_2O$	yellow wh.	insol.	insol.	Sol. in dil. acids.
Sulphate..$Fe_2(SO_4)_3.9H_2O$	red brown	very sol.	dec.	
Sulphocyan$Fe(SCN)_3\,3H_2O$	red	deliq.	deliq.	
Amm. Sulphate...$(24H_2O)$	white	14(20°)	400(100°)	Ferric ammon. alum.

Sol. in amm. chlor. : ferrous carbonate and hydrate.
Sol. in pot. cyan. (hot) : all insol. ferrous salts ; ferric cyanide, ferrocyan., and phosphate.
Sol. in tartrates : ferrous carbonate, hydrate, phosphate (diff. sol.) ; ferric cyanide, ferrocyan., hydrate, and phosphate.

OXIDATION AND REDUCTION.—Ferrous compounds are oxidized to ferric, by the oxygen of the air (hence reagent bottle of ferrous sulphate invariably contains ferric sulphate), by chromic acid, potassium permanganate, silver nitrate, chlorine, bromine, nitric acid, etc.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$
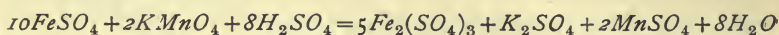
Ferric compounds are reduced to ferrous, by the action of iron, zinc, or tin, by stannous chloride, hydrogen sulphide, ammonium sulphide, dextrose, etc.

$$2FeCl_3 + (NH_4)_2S = 2FeCl_2 + 2NH_4Cl + S_*$$
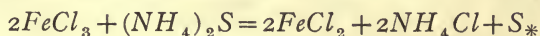
BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda, all compounds of iron are reduced to a black metallic powder attracted by the magnet. *Borax bead:* O.F., red, hot; yellow, cold; *R.F.*, colorless. *Microcosmic salt bead :* bottle green, hot; almost colorless, cold.

C H R O M I U M. $Cr = 51.77$.

OCCURRENCE.—*Ores:* chrome iron ore, $FeCr_2O_4$; crocoisite, $PbCrO_4$. *Metallurgy:* chrome iron ore, mixed with quicklime, is heated in a reverberatory furnace with free access of air, whereby calcium chromate is formed ; dilute sulphuric acid converts this into soluble dichromate, which with potassium carbonate yields red chromate of potash (potass. dichromate), from which all chromium compounds are obtained. *In commerce :* potassium (and sodium) dichromate, $K_2Cr_2O_7$; chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$; chrome yellow, $PbCrO_4$.

ATOMIC WEIGHT.—*Stoech. fig.:* 6.6595 grm. ; ammonium bichromate, upon heating, yielded 4.0187 grm. chromic oxide. *Specific heat,* 0.122. *Volatile compounds :* chromic trichloride, $CrCl_3$; chromous chloride, $CrCl_2$; chromium oxychloride, CrO_2Cl_2. *Isomorphous relations :* with sulphur and iron, in sulphates and ferrates ; with iron and aluminium, in alums, spinelles, and oxides (*cf.* iron).

CHEMICAL RELATIONS.—Chromium forms three series of compounds : chromous CrX_2, chromic CrX_3, and chromates.

The *chromous* compounds are very easily oxidized, *e.g.*, by the air—and are not met with in analysis. They resemble in chemical behavior, formulæ, and crystalline form, the corresponding ferrous compounds. The *chromic* compounds resemble those of the sesquioxides of aluminium, iron, manganese, and cobalt, there being a series of chromic alums and of members of the spinelles group. In their basicity the chromic hydrates stand between alumina and ferric hydrate, some forms being soluble and others insoluble in potash. The *chromates* correspond to the sulphates, the dichromates to the pyrosulphates (*not* to the bisulphates, or acid sulphates), chromium trioxide to sulphur trioxide, chromyl chloride to sulphuryl chloride, etc. The more metallic nature of chromium is evidenced by the existence of alkali chlorochromates undecomposed by cold water.

THE COMPOUNDS OF CHROMIUM.

NAME.	Color.	Solubility in 100 parts cold water.	Solubility in 100 parts hot water.	Remarks.
CHROMIC.				
Acetate ..... $Cr(C_2H_3O_2)_3$	....	very sol.	dec.	Basic acetate deposited.
Bromide .... $Cr\,Br_3$	dark gr.	very sol.	very sol.	Dissolves slowly.
Carbonate ....(basic)	red br.	insol.	insol.	
Chloride .... $Cr\,Cl_3$	dark red	very sol.	very sol.	Dissolves slowly.
Chromate.. .... $Cr\,O_2$	br. yel.	insol.	dec.	
Cyanide .... $Cr(CN)_3$	bl. grn.	insol.	insol.	S. ex. on warming.
Hydrate ... . $Cr(OH)_3$	pale bl.	insol.	insol.	Sol. cold potash.
Nitrate... $Cr\,(NO_3)_3 9H_2O$	purple	very sol.	very sol.	
Oxide.............. Cr_2O_3	green	insol.	insol.	Other oxides $Cr\,O_3$, $Cr\,O$.
Phosphate ...... $Cr_2(PO_4)_2$	green	insol.	insol.	
Sulphate $Cr_2(SO_4)_3.18H_2O$	violet	sol.	sol.	
Sulphide .... Cr_2S_3	grey grn.	insol.	insol.	Fuse hydrate and sulphur.
Chromyl chloride.. $Cr\,O_2Cl_2$	red	dec	dec.	
Pot. chrom....... $K_2Cr\,O_4$	yellow	50	60	
Pot. dichrom..... $K_2Cr_2O_7$	red	10	100	
Chrome alum	purple	14	....	Sol'n grn. on heating.

Sol. in pot. cyan.: all insol. chromic salts.
Sol. in tartrates : cyanide and hydrate.

Chromium is a light green, crystalline, difficultly fusible powder; *sp. gr.* 7.3, *m.p.* above that of platinum ; not oxidized in air at ordinary temperatures; heated in air, or in the presence of potash, it forms the oxide ; it dissolves readily in

dilute hydrochloric and sulphuric acids, but is insoluble in nitric acid.

Chromic compounds CrX_3, exist in two modifications in solution : green and violet ; only the latter crystallize.

Chromic chloride, $CrCl_3$; obtained by reducing potassium dichromate or chromic acid with hydrogen sulphide or alcohol in the presence of dilute hydrochloric acid. In the latter case the solution should be heated until the color changes to a pure green, after which the excess of acid and alcohol must be boiled off.

$$2K_2Cr_2O_7 + 6H_2S + 16HCl = 4CrCl_3 + 4KCl + 14H_2O + 3S_2$$
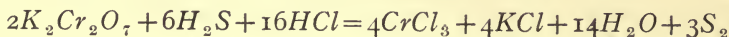
Chromic hydrate, $Cr(OH)_3$; precipitated from chromic salts (*e.g.*, chloride) by fixed alkalies, ammonia, alkali carbonates, barium carbonate, ammonium sulphide, or potassium cyanide. The precipitate is soluble in excess of cold alkali hydrate, almost insoluble in ammonia. The purple color sometimes observed in the filtrate from Group III A arises from the presence of small quantities of ammonium chromium double salts.

Chromyl chloride CrO_2Cl_2.—If equal quantities of finely divided potassium dichromate and sodium chloride be mixed, and heated with concentrated sulphuric acid in a test-tube provided with a cork and gas delivery tube, the latter dipping into caustic potash solution, brown vapors of chromyl chloride will distill over ; these react with the potash to form potassium chromate and potassium chloride.

Potassium chromite $KCrO_2$, in solution emerald green ; from chromic chloride by adding potash in sufficient excess (in the cold) to dissolve the precipitate at first formed. Upon boiling this solution, or by treating with acids, ammonium salts, or hydrogen sulphide, a chromic hydrate* is precipitated (*cf.* aluminium). With alkaline solution of zinc hydrate, zinc chromite $ZnCr_2O_4$, yellow, is precipitated.

Potassium chromate K_2CrO_4, from chromic hydrate or

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*The hydrate precipitated on boiling a dilute solution of potassium chromite contains less water than the " normal " hydrate, and is much less soluble.

oxide by fusing with a mixture of sodium nitrate and carbonate. With acids a red color is produced, arising from the formation of dichromates. The original color is restored by the addition of alkalies.

Chromium chromate $Cr_2O_3.CrO_3$, brown yellow; from chromic chloride with potassium chromate: consequently formed if potassium dichromate be partially reduced by hydrochloric acid and alcohol, and alkali be added.

OXIDATION AND REDUCTION.—Acid solutions of chromates or dichromates are reduced to chromic compounds (green) by almost all reducing agents, *e.g.*, sulphurous acids, sodium thiosulphate, hydrogen sulphide, alcohol, oxalic acid, ferrous and stannous salts, etc. Chromic compounds in alkaline solution, *i.e.*, as alkali chromites, can be oxidized to chromates by chlorine or bromine water, bleaching powder, lead dioxide, etc.

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda; chromium compounds are all reduced to chromic anhydride, Cr_2O_3, green. *Borax and microcosmic salt beads*: both flames, yellow green, hot; emerald green, cold.

SEPARATION IN GROUP III A.

Wash the precipitate of ferric, chromic, and aluminium hydrates, and boil for several minutes in a test-tube with a solution of potassium hydrate; filter.

Solution : potassium aluminate $KAlO_2$; from this a white, gelatinous precipitate of alumina may be obtained by barely acidifying with hydrochloric acid and adding ammonium carbonate.

Residue: $Fe(OH)_3$, $CrOH_3$. *Iron* may be detected by dissolving a part in dilute hydrochloric acid and adding potassium sulphocyanate or ferrocyanide; and chromium in another portion by oxidizing in alkaline solution, acidifying with acetic acid and adding lead acetate.

To oxidize the chromic hydrate it may be suspended in solution of potash and warmed with either bromine water, lead dioxide, or bleaching powder; or the hydrate may be fused with nitre and sodium carbonate, and the fused mass dissolved in water, and filtered (ferric hydrate separated).

COBALT. $Co = 58.4.$

OCCURRENCE.—*Ores :* cobalt glance, $(CoFe)AsS_2$; speiss cobalt, $(CoFeNi)As_2$; and almost always with nickel in the ores of the latter. *Metallurgy :* consult text-book. *In commerce :* smalt (silicate); Thénard's blue (aluminate) ; and cobalt nitrate, $Co(NO_3)_2 . 6H_2O.$

ATOMIC WEIGHT.—*Stoech. fig.* : upon reduction with hydrogen, 33.5908 grm. cobaltous oxide yielded 26.40 grm. metallic cobalt. *Specific heat*, 0.106. *Isomorphous relations :* with magnesium, zinc, iron, nickel, and manganese, in $MeSO_47H_2O$; with these, together with copper, cadmium, and mercury, in $MeSO_4.K_2SO_4.7H_2O$; with iron in $Me_3(PO_4)_3.8H_2O$, and with iron, aluminium, etc., in alums.

CHEMICAL RELATIONS.—Cobalt forms two series of salts : the cobaltous salts CoX_2, which resemble those of nickel to an extraordinary degree, correspond to the ferrous salts ; the hydrate, however, is a weaker base than the corresponding hydrate of iron, and from solutions of its salts potash in small quantity precipitates basic cobaltous salts, which, by continued action of water, may be converted into the hydrate. The cobaltic compounds CoX_3, with the exception of certain double salts (*e.g.*, cobaltic potassium nitrite and potassium cobalticyanide), are readily decomposed by water, and only a few of them have been obtained in the crystalline state. A very large number of ammonio-cobalt compounds are known. The metal itself is slightly magnetic.

THE COMPOUNDS OF COBALT.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
COBALTOUS.				
Acetate .... $Co\,(C_2H_3O_2)_2$	pink	deliq.	deliq.	
Bromide ... $Co\,Br_2.6H_2O$	red	deliq.	deliq.	
Carbonate......... $Co\,CO_3$	red	insol.	insol.	Basic : pink to violet.
Chloride .... $Co\,Cl_2.6H_2O$	red	sol.	sol.	Not deliquescent.
Chromate ....(basic)	red br.	insol.	insol.	
Cyanide........ $Co\,(CN)_2$	brown.	insol.	insol.	S. ex.
Ferrocyan ....$Co_2Fe\,(CN)_6$	grey grn.	insol.	insol.	Insol. dil. acids.
Ferricyan...$Co_3(Fe(CN)_6)_2$	br. red	insol.	insol.	Insol. dil. acids.
Hydrate........ $Cr\,(OH)_2$	pink	insol.	insol.	Insol. alkali hydrates.
Iodide........ $Co\,I_2.6H_2O$	dark grn.	very sol.	very sol.	
Nitrate.. $Co\,(NO_3)_2.6H_2O$	red	deliq.	deliq.	
Oxalate.......... $Co\,C_2O_4$	pink	insol.	insol.	
Oxide .... $Co\,O$	brown	insol.	insol.	Other oxides Cr_2O_3.
Phosphate$Co_3(PO_4)_2.8H_2O$	pink	insol.	insol.	$[Cr_3\,O_4$
Sulphate ....$Co\,SO_4.7H_2O$	red	4	65(70°)	
Sulphide .... $Co\,S$	black	insol.	insol.	Insol. amm. sulphide.
Sulphocyan.....$Co\,(SCN)_2$	blue	sol.	sol.	
Thiosulph .... $Co\,S_2O_3$	red	sol.	sol.	Not dec. on boiling.

Sol. in ammonia or in pot. cyan. : all insol. cobalt salts except sulphide.
Sol. in ammon. chlor. : carbonate, hydrate, and oxalate.
Sol. in tartrates : all insol. cobalt salts except ferrocyan., and sulphide.

Cobalt is a reddish grey, iridescent metal ; *sp. gr.* 8.6 ; *m.p.* 1800°C.; at ordinary temperatures not oxidized in the air ; as finely-divided powder it burns to form the oxide Co_3O_4. Dissolves readily in nitric, slowly in hydrochloric and sulphuric, acids.

Cobaltous compounds CoX_3, in solution, and hydrated crystals, red ; anhydrous crystals, lilac.

Cobaltous cyanide $Co(CN)_2$.—From solutions of cobaltous salts with potassium cyanide. The precipitate is soluble in excess of potassium cyanide, forming potassium cobalt cyanide $Co(CN)_2 . 2KN$, which, upon addition of a few drops of dilute hydrochloric acid and heating (with the excess of potassium cyanide), forms potassium cobalti-cyanide $K_3Co(CN)_6$. From this solution cobalt cannot be precipitated by dilute hydrochloric acid (distinction from nickel).

Potassium cobaltic nitrite.—From concentrated solutions of cobaltous salts (previously acidified by acetic acid), by addition of potassium nitrite. In dilute solutions the precipitate forms slowly (distinction from nickel, no precipitate).

$$[2Co(NO_3)_2 + 14KNO_2 + 4C_2H_4O_2 =$$
$$Co_2K_6(NO_2)_{12} + 4KNO_3 + 4KC_2H_3O_2 + 2NO + 2H_2O]$$
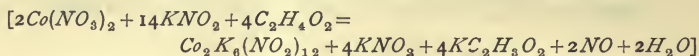
Cobalt ammonia compounds: cobaltamines.—A large class of variously colored compounds; from solutions of cobaltous salts by the addition of ammonia in sufficient excess to dissolve up the precipitate first formed. Treated with strong acids, or allowed to stand in the air, these solutions undergo change of color from formation of cobaltamines.

Potassium cobaltate, $[K_2Co_9O_{16}?]$—From oxides of cobalt by fusing with potash in the air. Insoluble in water, decomposed by acids.

OXIDATION AND REDUCTION.—In alkaline solution cobaltous compounds are oxidized to cobaltic by exposure to the air, by chlorine water, bromine water, potassium hypochlorite, lead dioxide, and by potassium nitrite in acetic acid solution. Cobaltic compounds are reduced to cobaltous by oxalic, phosphorous, sulphurous, hydrosulphurous, hydrochloric, etc., acids. Metallic cobalt is precipitated from solutions of cobalt salts on zinc, cadmium, and magnesium.

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda, all compounds of cobalt are reduced to a metallic powder attracted by the magnet. *Borax and microcosmic salt beads,* in both flames, blue, hot or cold.

NICKEL. $Ni=58.3$.

OCCURRENCE.—*Ores:* nickel blende, NiS; millerite, NiS_2; nickeline, $NiAs$; and almost always with cobalt in its ores. *Metallurgy:* consult text-book. *In commerce:* nickel matt; alloys, *e.g.,* German silver, armor-plates, etc.

ATOMIC WEIGHT.—*Stoech. fig.:* 28.5943 grm. nickel oxide yielded 22.4730 grm. metallic nickel. *Specific heat,* 0.109. *Isomorphous relations:* with magnesium, zinc, cobalt, iron, and

magnesium, in $MeSO_4.7H_2O$; with these together with copper, cadmium, and mercury in $MeSO_4.K_2SO_4.6H_2O$; with magnesium in $Me_2S_2O_3$.

CHEMICAL RELATIONS.—Nickel forms but one series of salts, of the type NiX_2, which strongly resemble the cobaltous salts ; from their solutions in water, however, potash does *not* precipitate basic salts. Ammonia-nickel compounds exist, but are formed much less readily than are the corresponding derivatives of cobalt. After iron, nickel has the greatest magnetic permeability.

THE COMPOUNDS OF NICKEL.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
Acetate.........$Ni(C_2H_3O_3)_2$	green	16	very sol.	
Bromide ......$Ni Br_2 . 2H_2O$	green	deliq.	deliq.	
Carbonate ....(basic)	green	insol.	insol.	Sol. amm. carb.
Chloride ....$Ni Cl_2 . 2H_2O$	green	sol.	sol.	Anhydrous, yellow.
Chromate ....(basic)	red br.	insol.	insol.	
Cyanide.......... $Ni (CN)_2$	grn. wh.	insol.	insol.	S. ex.
Ferrocyan ....$Ni_2Fe (CN)_6$	grn. wh.	insol.	insol.	Insol. dil. acids.
Ferricyan.....$Ni_3(Fe(CN)_6)_2$	grn. yel.	insol.	insol.	
Hydrate. .. ..$Ni(OH)_2$	pale grn.	insol.	insol.	Insol. alkali hydrates.
Iodide. ....$NiI_2 . 6H_2O$	green	deliq.	deliq.	
Nitrate .....$Ni(NO_3)_2 . 6H_2O$	green	50	very sol.	
Oxalate ....$Ni C_2O_4$	green	insol.	insol.	Sol. in amm. oxal.
Oxide .. .. $Ni O$	black	insol.	insol.	Other oxides Ni_2O_3.
Phosphate...$Ni_3(PO_4)_2 . 7H_2O$	green	insol.	insol.	Sol. dil. acids.
Sulphate ....$NiSo_4 . 7H_2O$	green	37	62 (70°)	Anhydrous, yellow.
Sulphide ....$Ni S$	black	insol.	insol.	S. sol. ammon. sulph.
Sulphocyan ..$Ni(SCN)_2 . \frac{1}{2}H_2O$	br. yel.	sol.	sol.	
Thiosulphate..$Ni_2S_2O_3 . 6H_2O$	green	sol.	dec.	Forms sulphide.

Sol. in ammonia, or in pot. cyan.: all insol. nickel salts except sulphide.
Sol. in ammon. chlor.: carbonate, hydrate, oxalate, and phosphate.
Sol. in tartrates : all insol. nickel salts except ferrocyan. and sulphide.

Nickel is a silver-white, lustrous, malleable metal ; *sp. gr.* 8.82, *m.p.* 1500° C. In air at ordinary temperatures unchanged ; heated, forms nickel oxide ; dissolves readily in dilute nitric acid, slowly in dilute hydrochloric and sulphuric acids ; insoluble in concentrated nitric acid (*cf.* iron).

Nickelous compounds, NiX_2 : dilute solutions and hydrated crystals, green ; anhydrous crystals, yellow.

Nickel cyanide, $Ni(CN)_2$: from solutions of nickel salts with potassium cyanide ; precipitate soluble in excess $(KCN)_2$ $Ni(CN)_2$, reprecipitated upon addition of a few drops of dilute hydrochloric acid (*cf.* cobalt).

Nickel hydrate, $Ni(OH)_2$: from solutions of nickel salts with alkali hydrates or ammonia ; soluble in excess of ammonia, forming compounds which, upon exposure to the air, show a change of color similar to that of the cobaltamines. From these solutions the nickel can be slowly reprecipitated by potassium or sodium hydrate (distinction from cobalt).

OXIDATION AND REDUCTION.—In alkaline solution nickelous compounds are oxidized to nickelic oxide by chlorine water, bromine water, sodium hypochlorite, and sodium hypobromite. Nickelic oxide is reduced to nickelous by oxalic, nitrous, phosphorous, sulphurous, hydrochloric, hydrobromic, hydroferrocyanic, etc., acids. Nickel compounds deposit metallic nickel upon zinc, cadmium, tin, etc.

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda, all compounds of nickel are reduced to a metallic black powder attracted by the magnet. *Borax bead:* O. F., purplered or violet, hot ; yellow brown, cold. R. F., grey or colorless. *Microcosmic salt bead* : both flames, reddish brown, hot ; reddish yellow, cold.

MANGANESE.   *Mn* = 54.53.

OCCURRENCE.—*Ores* : pyrolusite, MnO_2 ; braunite, Mn_2O_3 ; manganite or wad, $(MnO)OH$; hausmanite, Mn_3O_4 ; manganese spar, $MnCO_3$; in almost all ores of iron, and in many silicates, coloring them. *Metallurgy* : the metal is obtained with difficulty from the oxides by reduction with charcoal. *In commerce* : black oxide of manganese, MnO_2 ; potassium permanganate, $KMnO_4$; and in alloys, *e.g.*, manganese bronze.

ATOMIC WEIGHT.—*Stoech. fig.*: (i.) 80.5661 grm. silver permanganate required 42.2506 grm. potassium bromide to convert it into silver bromide ; (ii.) 10.6730 grm. manganese oxide yielded 22.6875 grm. manganese sulphate. *Specific heat,*

0.109.   *Isomorphous relations* : with magnesium, zinc, iron, nickel, and cobalt, in $MeSO_4.7H_2O$; with these, together with copper, cadmium, zinc, and mercury in $MeSO_4.K_2SO_4.6H_2O$; with iron and chromium in the alums and in Me_2O_3 ; with iron and aluminium, in $MeO(OH)$; with iron, chromium, and sulphur in K_2MeO_4 ; and with chlorine in $KMeO_4$.

CHEMICAL RELATIONS.—Manganese forms six series of salt. *Manganous*, MnX_2, resembling ferrous salts ; *manganic*, MnX_3, like cobaltic salts, easily decomposed by heat and on boiling with water (only a few, *e.g.*, the sulphate and phosphate, have been obtained in the crystalline form) ; *manganese tetrachloride*, bromide, etc., MnX_4, obtained by the action of the corresponding acids on manganese dioxide, and known only in solution (a double salt, $MnF_4.2KF$, has been obtained in the solid form) ; the *manganites*, *e.g.*, $CaMn_5O_{11}$, prepared by the action of bleaching powder on manganous nitrate ; the *manganates*, *e.g.*, KMn_2O_4, corresponding to the chromates and sulphates, from manganese dioxide by fusing with potash and nitre ; these latter are soluble in water containing potash, but decomposed by pure water with precipitation of manganic hydrate and formation of the *permanganates*, *e.g.*, $KMnO_4$, corresponding to the perchlorates.

THE COMPOUNDS OF MANGANESE.

Manganese is a greyish-white, brittle, difficultly fusible metal, *sp.gr.* 7.2, *m.p.* 1900° C.; oxidizes readily in the air at ordinary temperatures and decomposes water without heating. It dissolves readily in dilute acids.

Manganous compounds.—MnX_2 ; colorless or slightly pink in solution.

Manganous carbonate, $MnCO_3$: precipitated from solutions of manganous salts by alkali carbonates ; in air oxidizes to form brown manganic oxyhydrate $MnO(OH)$.

Manganous cyanide, $Mn(CN)_2$: precipitated from manganous solutions by potassium cyanide ; soluble in excess of alkali cyanide to form the double cyanide $Mn(CN)_2.2KCN$;

exposed to the air potassium *manganicyanide* is formed (*cf.* iron and cobalt).

$$12(KCN)_2Mn(CN)_2 + 3O_2 + 2H_2O = 8K_3Mn(CN)_6 + 4MnO(OH)$$
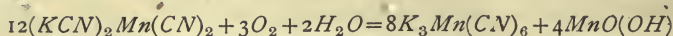
Manganous hydrate, $Mn(OH)_2$: precipitated from manganous salts by fixed alkali hydrates; soluble in ammonium salts with formation of ammonio-manganous compounds, from which, exposed to the air, manganic oxyhydrate $MnO.OH$, brown, gradually separates.

Manganous sulphide, $MnS.H_2O$: precipitated from manganous and *manganic* solutions by ammonium sulphide. With excess of ammonia and absence of ammonia salts a green precipitate $3\ MnS . 2H_2O$ is formed.

NAME.	Color.	Solubility in 100 parts water.		Remarks.
		cold	hot	
MANGANOUS.				
Acetate ... $Mn(C_2H_3O_2)_2$	pink	$30(15°)$	very sol.	
Bromide . .$Mn\ Br_2.4H_2O$	pink	deliq.	deliq.	
Carbonate........$Mn\ CO_3$	pink	0.01	s. sol.	Sol. amm. carb.
Chloride.....$Mn\ Cl_2.4H_2O$	pink	sol.	650	
Chromate ......$Mn\ CrO_4$	brown	insol.	insol.	
Cyanide........$Mn(CN)_2$	brown	insol.	insol.	S. ex.
Ferrocyan ...$Mn\ Fe(CN)_6$	white	insol.	insol.	Insol. dil. hydrochl. acid
Ferricyan .$Mn_3(Fe(CN)_6)_2$	brown	insol.	insol.	
Hydrate ....$Mn(OH)_2$	white	insol.	insol.	Brown on standing.
Iodide ....$Mn\ I_2.4H_2O$	pink	deliq.	deliq.	Decomposes in air.
Nitrate..$Mn(NO_3)_2.6H_2O$	white	deliq.	deliq.	
Oxalate.........$Mn\ C_2O_4$	pink	0.04	0.1	S. sol. ex.
Oxide.............$Mn\ O$	green	insol.	insol.	Other ox.$Mn_3O_4,MnO_2,$
Phosphate .....$Mn_3(PO_4)_2$	white	s. sol.	s. sol.	Sol. dil. acids. [Mn_2O_7.
Sulphate....$Mn\ SO_4.7H_2O$	pink	very sol.	very sol.	Also $MnSO_4.SH_2O$.
Sulphide .... $Mn\ S$	green	insol.	insol.	Hydrated sulphide, flesh
Thiosulph ......$Mn_2S_2O_3$	white	deliq.	dec.	Forms sulphide. [color.
MANGANIC.				
Hydrate ....$Mn_2O_2(OH)_2$	brown	sol.	insol.	
Phosphate ...$Mn\ PO_4.H_2O$	pink	s. sol.	sol.	
Sulphate ......$Mn_2(SO_4)_3$	green	dec.	dec.	
Pot. Permang..... $K\ Mn\ O_4$	violet	6.5	very sol.	

Sol. in ammon. chlor. : hydrate, cyanide, chromate, and carbonate.
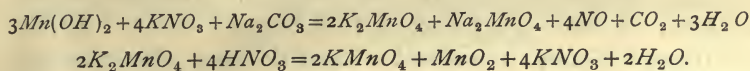Sol. in pot. cyan. : cyanide and carbonate.
S. tartrates : hydrate, cyanide, chromate, and carbonate.

Manganic compounds, MnX_3 : purple-red in solution.
Manganates, green, soluble in water. In alkaline solution

manganates remain unchanged ; treated with dilute nitric or sulphuric acid they rapidly undergo transformation into permanganates (violet).

$$3Mn(OH)_2 + 4KNO_3 + Na_2CO_3 = 2K_2MnO_4 + Na_2MnO_4 + 4NO + CO_2 + 3H_2O$$
$$2K_2MnO_4 + 4HNO_3 = 2KMnO_4 + MnO_2 + 4KNO_3 + 2H_2O.$$

OXIDATION AND REDUCTION.—Manganous compounds may be oxidized to manganic upon heating, or upon simple exposure to the air, *e.g.*, hydrate, carbonate, cyanide, etc. Manganous compounds are oxidized to manganates and permanganates by fusion with carb. soda and potassium chlorate or nitrate ; by heating in alkaline solution with bromine, or in acid solution with red lead.* Manganous compounds are oxidized to manganites by solution of bleaching powder. Manganic compounds are reduced to manganous by warming with acids. Permanganates and manganates are reduced to manganous compounds by ferrous sulphate, oxalic acid, sodium thiosulphate, alcohol, etc., in acid solution ; permanganates to manganates and finally to manganese dioxide by alkaline solutions of alcohol, stannous chloride, etc.

BLOWPIPE REACTIONS.—All manganese compounds, fused with carb. soda on a platinum wire, yield a green-colored bead (turquoise enamel). *Borax and microcosmic salt beads*; O. F., violet, hot ; amethyst-red, cold ; R. F., slowly decolorized.

ZINC. Zn = 64.77.

OCCURRENCE.—*Ores*: zinc blende, ZnS ; smithsonite, $ZnCO_3$; and siliceous calamine, $ZnSiO_4 . H_2O$. *Metallurgy*: the metal is obtained from zinc blende by roasting (to convert the sulphide into oxide), and subsequent reduction with charcoal. *In commerce*: metal; alloys, *e.g.*, brass, bronze, etc.; white vitriol, $ZnSO_4 . 7H_2O$; zinc chloride, $ZnCl_2$; and zinc white, ZnO.

---

* Mix a little red lead with 5-10 *cc.* dil. nitric acid in a test-tube, heat almost to boiling and add a drop of dilute solution of manganous sulphate. Very delicate test for manganese if properly carried out. Essential to the success of the experiment is the absence of all reducing agents (*e.g.*, hydrochloric acid, excess of manganous salt).

ATOMIC WEIGHT.—*Stoech. fig.*: (i.) 29.6754 grm. zinc dissolved in dilute sulphuric acid evolved 10.0934 litres hydrogen at normal temperature and pressure; (ii.) 16.0316 grm. zinc yielded 20.2608 grm. zinc oxide; (iii.) electrolytically, one grm. of zinc is equivalent to 3.30 grm. silver. *Specific heat,* 0.094. *Volatile compounds*: metallic zinc, zinc chloride, and zinc organic compounds. *Isomorphous relations*: with cadmium in *MeS*; with beryllium in $MeSiO_4$; with magnesium, calcium, iron, and manganese, in $MeCO_3$; with magnesium, iron, nickel, cobalt, and manganese, in $MeSO_4 . 7H_2O$; with copper, magnesium, cadmium, mercury, iron, nickel, cobalt, manganese, and chromium, in $MeSO_4 . K_2SO_4 . 6H_2O$; and with iron and magnesium in the spinelles.

CHEMICAL RELATIONS.—With acids, zinc forms salts of the type ZnX_2, many of which are isomorphous with the corresponding salts of magnesium, chromium, manganese, iron, cobalt, and nickel; the chloride is partially decomposed on boiling with water, and the hydrate dissolves in solutions of potash or soda forming alkali *zincates*. Though strongly resembling magnesium, zinc is one of the heavy metals (*sp. gr.* 7.5), and correspondingly its hydrate and sulphide are insoluble in water, and its oxide is easily reduced by carbon.

THE COMPOUNDS OF ZINC.

Zinc is a bluish white metal, *sp. gr.* 7.14, *m.p.* 450°C.; not oxidized in air at ordinary temperatures; heated in air forms zinc oxide; if impure, it dissolves readily in dilute acids, very slowly in concentrated nitric acid. (The solution of pure zinc in dilute acids may be hastened by touching it with a strip of copper or platinum standing in the acid, or by adding copper sulphate to the solution. Solution of the pure metal in fixed alkalies is promoted by presence of iron filings.)

Zinc compounds, MX_2: colorless in solution, except the acid be colored.

Potassium zincate, K_2ZnO_2, white: from solutions of zinc salts by potash in sufficient excess to dissolve the precipitate,

$Zn(OH)_2$, first formed.   Dilute solutions of zincates on boiling precipitate zinc oxide; concentrated solutions are not decomposed by heat.

NAME.	Color.	Solubility in 100 parts cold / hot water.		Remarks.
Acetate . . . . . . $Zn\ (C_2H_3O_2)_2$	white	30	200	
Bromide . . . . $Zn\ Br_2$	white	deliq.	deliq.	
Carbonate . . . . (*basic*)	white	0.005	insol.	S. sol. amm. carb.
Chloride . . . . $Zn\ Cl_2$	white	300	very sol.	*B. P.* 400° *C.*
Chromate . . . . (*basic*)	yellow	s. sol.	s. sol.	
Cyanide . . . . $Zn\ (CN)_2$	white	insol.	insol.	S. ex.
Ferrocyan . . . . $Zn_2Fe\ (CN)_6$	white	insol.	insol.	S. sol. dil. hydrochl acid.
Ferricyan . . . $Zn_3(Fe(CN)_6)_2$	yellow	insol.	insol.	Sol. dil. hydrochlor. acid.
Hydrate . . . . $Zn\ (OH)_2$	white	insol	insol.	Sol. alkali hydrates.
Iodide . . . . $Zn\ I_2$	white	deliq.	deliq.	
Nitrate . . . $Zn\ (NO_3)_2.6H_2O$	white	deliq.	deliq.	
Oxalate . . . . $Zn\ C_2O_4$	white	insol.	insol.	
Oxide . . . . $Zn\ O$	white	0.001	insol.	
Phosphate . . . . $Zn_3(PO_4)_2$	white	insol.	insol.	Sol. dil. acids.
Sulphate . . . . . $Zn\ SO_4.7H_2O$	white	135	655	" White vitriol."
Sulphide . . . . $Zn\ S$	white	insol.	insol.	Insol. dil. acetic acid.
Sulphocyan . . . . . . $Zn\ (SCN)_2$	white	very sol.	very sol.	
Thiosulph . . . . $Zn\ S_2O_3.H_2O$	white	deliq.	dec.	Forms sulphide.

Sol. in ammonia : all insol. zinc salts except sulphide and ferrocyanide.
Sol. in pot. cyan. : all insol. zinc salts except sulphide, ferrocyan. and hydrate.
Sol. in tartrates : all insol. zinc salts except sulphide, ferrocyan. and phosphate.
Sol. in ammon. chlor. : all insol. zinc salts except sulphide, ferocyan. and phosphate

BLOWPIPE REACTIONS.—*B. B. on C.* with carb. soda, compounds of zinc are reduced to metallic state.   The metal oxidizes to form an incrustation on the charcoal, yellow when hot, white when cold ; moistened with cobalt nitrate and re-ignited, the incrustation assumes a green color.

SEPARATION IN GROUP III B.

Treat the washed precipitate of the sulphides of nickel, cobalt, manganese, and zinc with cold dilute* (three per cent.) hydrochloric acid.   Filter.

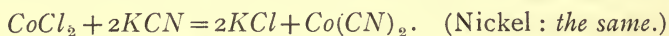> *Black residue* (soluble in aqua regia): NiS, CoS; detected by blowpipe.
>
> *Solution*, $MnCl_2$, $ZnCl_2$.—Add potash in excess and digest without warming.   Filter.
>
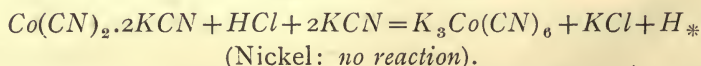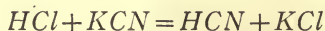>> *Precipitate* $Mn(OH)_2$.—Oxidize to permanganic acid by red lead and nitric acid.
>>
>> *Solution* K_2ZnO_2.—Ammonium sulphide gives white precipitate of zinc sulphide.

To separate nickel and cobalt several methods are employed, all depending on the fact that cobalt forms salts derived from the sesquioxide, while nickel does not. Of these the most convenient is that with potassium cyanide, involving the formation of potassium cobalticyanide, as follows :—

To the solution containing salts of nickel and cobalt (*e.g.*, $NiCl_2$ and $CoCl_2$), add potassium cyanide in quantity slightly more than sufficient to dissolve the precipitate first formed : —

$$CoCl_2 + 2KCN = 2KCl + Co(CN)_2. \quad \text{(Nickel : } the same.\text{)}$$

$$Co(CN)_2 + 2KCN = Co(CN)_2.2KCN. \quad \text{(Nickel : } the same.\text{)}$$
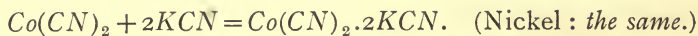
Add a few drops of dilute hydrochloric acid and boil a minute :

$$HCl + KCN = HCN + KCl$$

$$Co(CN)_2.2KCN + HCl + 2KCN = K_3Co(CN)_6 + KCl + H_*$$
$$\text{(Nickel: } no reaction\text{)}.$$

*One part of the reagent solution "dilute hydrochloric acid" and two parts of

To the solution add dilute hydrochloric acid drop by drop: the potassium cobalticyanide forms soluble cobalticyanic acid; while the nickel is precipitated as cyanide, soluble in excess of hydrochloric acid

$$Ni(CN)_2.2KCN + 2HCl = Ni(CN)_2 + 2HCN + 2KCl$$
$$Ni(CN)_2 + 2HCl = NiCl_2 + 2HCN$$
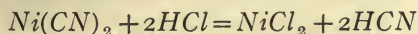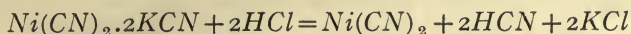
Or, to the solution of potassium cobalticyanide and nickel potassium cyanide, add a little potash and then bromine water: nickel is precipitated as the black nickelic hydrate $Ni(OH)_3$, while the cobalticyanide is not decomposed.

Nickel may be detected in the presence of cobalt by the following reactions, which, however, do not lead to a separation of the two elements.

To the solution of the chlorides, add ammonium chloride, ammonia and potassium ferricyanide: a blood-red color (due to the formation of a cobaltamine compound) indicates cobalt; if the mixture be boiled, the presence of nickel will be shown by the formation of a copper-red precipitate.

ANALYSIS OF GROUP III IN PRESENCE OF PHOSPHATES, ETC.

The composition of the precipitate formed by the third group reagents, is modified by the presence of certain substances: tartaric acid, citric acid, and many other non-volatile organic substances (especially those whose structural formulæ contain the hydroxyl group, for instance sugar), hinder, and, if present in sufficient quantity, completely prevent the precipitation of alumina and chromic and ferric hydrates; while phosphoric and oxalic acid, as soon as the solution is made alkaline by ammonia, bring about a precipitation of calcium, strontium, barium, and magnesium as phosphates or oxalates respectively. For this reason it is necessary, first of all, to

make a preliminary investigation as to the presence or absence of these substances, according to the scheme given in the chapter on the detection of the acids. If they be present, they may be removed as follows before proceeding with the analysis:

To remove organic substances: the filtrate from Group II is evaporated to dryness and then *gently* ignited in a porcelain crucible, and the residue dissolved in hydrochloric acid; or, if phosphorus be present, in nitric acid, filtered and analyzed according to the usual method.

To remove phosphoric acid: the nitric acid solution is warmed in an evaporating dish with granulated tin, or better tin-foil, and excess of nitric acid, until a portion tested with ammonium molybdate shows the absence of phosphoric acid. [As the nitric acid evaporates it must be replaced; if this be not attended to, aluminium, chromium, and iron may go into the precipitate.] The whole is then heated for a moment to boiling, the solution poured off from the precipitate, diluted with water, lead (from the tin-foil) precipitated by hydrogen sulphide, filtered, and the filtrate examined for Group III as usual.

To analyze the precipitate produced by the third group reagents in a solution containing phosphoric acid:

Wash separately the precipitates of Group III A and Group III B, mix them, and warm them with ammonium sulphide. Filter and wash. The precipitate may contain the *sulphides* of iron, manganese, cobalt, nickel, and zinc, the *hydrates* of aluminium and chromium, and the *phosphates* of aluminium, chromium, calcium, strontium, barium, and magnesium.

Dissolve this precipitate in hot dilute hydrochloric acid with addition of a crystal of potassium chlorate, remove chlorine by boiling and any sulphur by filtration; add sodium carbonate until a precipitate is produced, then just enough dilute hydrochloric acid to dissolve it again, and, lastly, excess of sodium acetate solution slightly acidified with acetic acid. Warm for some time and filter hot.

Precipitate $FePO_4$, $AlPO_4$, $CrPO_4$. The iron and chro-

mium may be detected as described on page 89 ; the aluminium by boiling the precipitate with potassium hydrate for some minutes, filtering, acidifying the filtrate with hydrochloric acid and adding excess of ammonia, which causes a white precipitate of aluminium phosphate insoluble in acetic acid.

Filtrate, $CoCl_2$, $NiCl_2$, $MnCl_2$, $ZnCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$. $MgCl_2$, and *either* $FeCl_3$, $CrCl_3$ and $AlCl_3$ *or* H_3PO_4, Add ferric chloride drop by drop so long as a precipitate results and until the liquid turns red, and digest for a time at a gentle heat. Remove the precipitate $FePO_4$ by filtration. To the filtrate, or solution not precipitated by ferric chloride, add amonium chloride etc., proceeding as directed on page 89.

THE FOURTH GROUP.

Barium, strontium, and calcium, the metals of this group, resemble one another so closely that it is more satisfactory to treat of the chemical relations of all three together in this place than to consider each one under a separate head. In Mendelejeff's table they are the next-door neighbors of the alkali metals, and resemble the latter in their power of decomposing cold water, in being readily oxidized in the air, and in the strongly basic properties of their hydrates; they differ in forming insoluble carbonates, sulphates, and phosphates.

Of the three hydrates, that of barium is the strongest base; it may be melted at a red heat without losing water, and the carbonate of barium gives off but little carbon dioxide at its melting temperature—contrast the corresponding compounds of calcium. Strontium in this, as in other respects, (for instance, in the solubilities of its salts) stands midway between the other two.

Each of these metals forms only one series of salts; but as none of the latter are volatile enough to admit of a vapor density measurement, and as, until recently, no specific heat determination of any of the metals themselves had been made, the atomic weights of the elements could be deduced only from a study of their isomorphous relations. In order to show their analogy, from a crystallographic point of view, with the members of the magnesium group, the salts of barium, strontium, and calcium have been given the general formula MX_2. The atomic weights thus decided on have been confirmed by a subsequent determination of the specific heat of calcium.

Barium, strontium, calcium, and magnesium are termed the "alkaline earths," standing intermediate between the alkalies on the one hand, and the "true earths," *e.g.*, alumina,

on the other. Magnesium, however, by reason of the solubility of its carbonate in ammonia salts, is separated from the others in the scheme of analysis adopted, and has a place in the fifth analytical group.

BARIUM. $Ba = 136.40.$

OCCURRENCE.—*Ores*: heavy spar, $BaSO_4$; and witherite, $BaCO_3$. *Metallurgy*: the metal is obtained by electrolysis of the chloride, or by reducing the latter with sodium or potassium. *In commerce*: permanent white (paint), $BaSO_4$; barium nitrate, $Ba(NO_3)_2$; barium dioxide, BaO_2 (manufacture of hydrogen peroxide).

ATOMIC WEIGHT.—*Stoech. fig.*: 124.1929 grm. barium chloride convert 128.8934 grm. silver into silver chloride. *Isomorphous relations*: with calcium, strontium, and lead, in $MeCO_3$ (arragonite series), and in $MeSO_4$.

THE COMPOUNDS OF BARIUM.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
Acetate..$Ba(C_2H_3O_2)_2.2H_2O$	white	80 (15°)	90 (100°)	
Bromide ......$BaBr_2 . 2H_2O$	white	100	150	
Carbonate ....$BaCO_3$	white	insol.	insol.	
Chloride .. ....$BaCl_2.2H_2O$	white	33 (10°)	60 (104°)	
Chromate ....$BaCrO_4$	yellow	insol.	insol.	Sol. chromic acid (*cf.* lead).
Cyanide...........$Ba(CN)_2$	white	s. sol.	sol.	
Ferrocyan. ....$Ba_2Fe(CN)_6$	white	0.1	0.85	
Ferricyan ....$Ba_3(Fe(CN)_6)_2$	white	s. sol.	sol.	
Hydrate ....$Ba(OH)_2 .8H_2O$	white	1.7(0°)	101. (80°)	
Iodide.........$BaI_2 . 2H_2O$	white	200	300	
Nitrate...........$Ba(NO_3)_2$	white	5	35 (102°)	
Oxalate ....BaC_2O_4	white	0.4	0.4	S. sol. amm. chl.
Oxide ....BaO	white	....	....	With water forms hydrate.
Phosphate ....$BaH(PO_4)$	white	insol.	insol.	$Ba_3(PO_2)_2$ on standing.
Sulphate ....$BaSO_4$	white	0.0003	insol.	Insol. dil. acids.
Sulphide ....BaS	white	dec.	dec.	$BaS.6H_2O$ dissolves undec.
Sulphocyan . .....$Ba(SCN)_2$	white	deliq.	deliq.	
Thiosulph ....BaS_2O_3	white	s. sol.	sol.	

Barium is a silver white or yellow powder, *sp. gr.* 3.6, *m.p.* red heat; oxidizes rapidly in the air at ordinary temperatures; decomposes water readily with evolution of hydrogen.

Barium compounds, BaX_2, colorless in solution, except when the acid is colored.

OXIDATION AND REDUCTION.—At red heat in air barium oxide and hydroxide form barium peroxide; at a white heat the peroxide loses oxygen to form barium oxide.

FLAME TEST.—Moistened with dilute hydrochloric acid, all barium compounds impart a green color to the flame.

STRONTIUM. $Sr = 87.00$.

OCCURRENCE.—*Ores* : strontianite, $SrCO_3$; coelestine, $SrSO_4$.   *Metallurgy* : metal obtained by electrolysis of the chloride, or by reduction of this salt with sodium.   *In commerce* : strontium carbonate (sugar refineries).

ATOMIC WEIGHT.—*Stoech. fig.* : (i.) 2.9718 grm. strontium chloride, converted 4.0493 grm. silver into silver chloride ; (ii.) 10.00 grm. strontium chloride yielded 6.8855 grm. strontium sulphate.   *Isomorphous relations* : with calcium, barium, and lead, in $MeCO_3$, and $MeSO_4$.

THE COMPOUNDS OF STRONTIUM.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
STRONTIUM.				
Acetate ....$Sr (C_2H_3O_2)_2$	white	40	40	
Bromide.... $Sr Br_2.6H_2O$	white	88 (0°)	250(110°)	
Carbonate .... $Ba CO_3$	white	0.006	insol.	Sol. in water containing
Chloride ......$Sr Cl_2.6H_2O$	white	44	117(118°)	[CO_2.
Chromate ....$Sr Cr O_4$	yellow	s. sol.	sol.	Sol. in acetic acid.
Cyanide ....$Sr (CN)_2$	white	insol.	insol.	
Ferrocyan.....$Sr_2Fe(CN)_6$	white	50	100	
Ferricyan . $Sr_3(Fe(CN)_6)_2$	white	sol.	sol.	
Hydrate . $Sr (OH)_2.8H_2O$	white	2 (10°)	40(100°)	Sol. in tartrates.
Iodide........$Sr I_2.6H_2O$	white	sol.	sol.	
Nitrate ..$Sr(NO_3)_2.4H_2O$	white	40	103(108°)	
Oxalate ....$Sr C_2O_4$	white	insol.	insol.	
Oxide ....$Sr O$	white	s. sol.	s. sol.	Other oxide $Sr O_2$.
Phosphate ......$SrHPO_4$	white	insol.	insol.	$Sr_3(PO_4)_2$ on standing.
Sulphate ....$Sr SO_4$	white	0.015(0°)	0.01(100°)	S. sol. dil. acids.
Sulphide ......$Sr S$	white	dec.	dec.	
Sulphocyan.... $Sr (SCN)_2$	white	deliq.	deliq.	
Thiosulph ....$Sr S_2O_3$	white	27(16°)	57(100°)	

Strontium is a light yellow metal, *sp.gr.* 2.5, *m.p.* red heat ; oxidizes in the air at ordinary temperatures, forming strontium oxide ; decomposes water without heating.

Strontium compounds, SrX_2, are colorless in solution except when the acid is colored.

OXIDATION.—*Strontium oxide* forms the peroxide by heating in a current of oxygen, or by treating with hydrogen peroxide.

FLAME TEST.—All strontium compounds, moistened with dilute hydrochloric acid, impart a carmine red color to the flame.

CALCIUM. $Ca = 39.71.$

OCCURRENCE.—*Ores*: limestone or marble (calcite), $CaCO_3$; arragonite, $CaCO_3$; gypsum, $CaSO_4.2H_2O$; fluor spar, CaF_2; and apatite, $Ca_3(PO_4)_2 + CaCl_2$;   *Metallurgy*:   the metal is obtained by electrolysis of the chloride, or by fusing the latter with sodium.   *In commerce* : marble, $CaCO_3$; quicklime, CaO ; plaster of paris, $Ca SO_4$; superphosphate of lime, $CaH_4(PO_4)_2$ mixed with calcium sulphate ; and bleaching powder, $CaCl.OCl$ or $Ca(OCl)_2 + CaCl_2$.

ATOMIC WEIGHT.—*Stoech. fig.* : (i.) 10.00 grm. calcium carbonate yielded 13.6050 grm. calcium sulphate.   (ii.) 6.870 grm. calcium chloride, converted 13.3640 grm. silver into silver chloride. *Specific heat*, 0.170. *Isomorphous relations* : with strontium, barium, and lead in $MeCO_3$, and $MeSO_4$;   with lead in $3Me_3(PO_4)_2.MeCl_2$, and $MeWO_4$.

THE COMPOUNDS OF CALCIUM.

Calcium is a yellow lustrous metal, *sp. gr.* 1.6, *m. p.* red heat. In dry air at ordinary temperatures it is slowly oxidized ; it burns to form calcium oxide CaO; decomposes water in the cold.

Calcium compounds, CaX_2 ; colorless in solution, except when the acid is colored.

Calcium arsenite, $CaHAsO_3$, white ; from solutions of calcium salts slowly precipitated by ammonium arsenite. (Distinction from barium and strontium, no precipitate.)

Calcium hypochlorite, $Ca(OCl)_2$: obtained by passing chlorine gas into a milky solution of calcium hydroxide :—

$$2Ca(OH)_2 + 2Cl_2 = 2Ca(OCl)_2 + CaCl_2 + H_2O$$
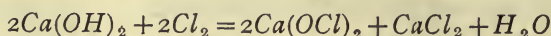
The resulting mixture of hypochlorite and chloride of calcium constitutes the bleaching powder of commerce. Its use as a disinfectant and oxidizing agent depends upon the evolution of chlorine when treated with diluted acids, *e.g.* :—

$$Ca(OCl)_2 + 4HCl = CaCl_2 + 2Cl_2 + 2H_2O.$$

NAME.	Color.	Solubility in 100 parts water. cold	hot	Remarks.
CALCIUM.				
Acetate.....$Ca\ (C_2H_3O_2)_2$	white	17(12°)	very sol.	
Bromide..........$Ca\ Br_2$	white	125(0°)	300(100°)	
Carbonate ....$Ca\ CO_3$	white	0.002	0.09	Sol. in ammon. chloride.
Chloride ....$Ca\ Cl_2.6H_2O$	white	400	650	
Chromate ....$Ca\ Cr\ O_4$	yellow	very sol.	very sol.	
Cyanide ....$Ca\ (CN)_2$	white	sol.	sol.	
Ferrocyan ....$Ca_2Fe(CN)_6$	white	sol.	sol.	
Ferricyan. $Ca_3(Fe(CN)_6)_2$	white	sol.	sol.	
Hydrate.... ....$Ca\ (OH)_2$	white	0.13	0.075	Sol. in tartrates and
Iodide... ....$Ca\ I_2$	white	deliq.	deliq.	[ammon. chlor.
Nitrate...$Ca\ (NO_3)_2.4H_2O$	white	very sol.	very sol.	
Oxalate ....$Ca\ C_2O_4$	white	insol.	insol.	Other oxide, $Ca\ O_2$.
Oxide ....$Ca\ O$	white	0.13	0.08	$Ca_3(PO_4)_2$ on standing.
Phosphate ......$CaH(PO_4)$	white	insol.	insol.	Max. solubility at 38°.
Sulphate ....$Ca\ SO_4.2H_2O$	white	0.25 (0°)	0 22(100°)	
Sulphide ....$Ca\ S$	white	0.2	dec.	
Sulphocyan ....$Ca\ (SCN)_2$	white	deliq.	deliq.	
Thiosulph...$CaS_2O_3.6H_2O$	white	100	dec.	

OXIDATION.—Calcium oxide may be converted into the peroxide by treating with hydrogen peroxide.

FLAME TEST.—Moistened with dilute hydrochloric acid, all calcium compounds impart a yellowish red color to the flame.

SEPARATION IN GROUP IV.

Note.—(i.) If the filtrate from Group III contain much ammonium sulphide, this must be decomposed by dilute hydrochloric acid and the sulphur filtered off, before adding the fourth group reagents.

(ii.) The carbonates of Group IV are not absolutely insoluble in ammonium chloride; addition of ammonia and an excess of ammonium carbonate greatly lessens the amount dissolved.

To remove Barium: (*a*) Dissolve the precipitate of carbonates in dilute acetic acid; to part of the solution add potassium dichromate, a yellow precipitate, $BaCrO_4$, indicates the presence of barium, and the reagent must be added to the whole solution.

(*b*) Dissolve the carbonates in dilute hydrochloric acid, remove the excess of acid by evaporating to dryness, dissolve in a little water, and precipitate by dil. sulphuric acid. The precipitate, $BaSO_4$, $SrSO_4$, $CaSO_4$, must be digested with sodium carbonate solution for ten minutes at $100°$ C., filtered, washed, and treated with dilute nitric acid.

Residue: barium sulphate (free from Sr and Ca).

Solution: nitrates of strontium and calcium.

Detection of Strontium in the absence of Barium: To a portion of the solution of the chlorides free from acid (see last paragraph) add calcium sulphate, boil, and let stand for ten minutes. *Precipitate*: strontium sulphate.

Detection of Calcium in the presence of Barium and Strontium: Precipitate the neutral solution of the chlorides with dilute sulphuric acid, filter, and to the filtrate add ammonia and ammonium oxalate. *Precipitate*: calcium oxalate.

THE FIFTH GROUP.

Commoner elements: $Mg, K, Na, [NH_4]$.
Rarer elements: Li, Rb, Cs.

Magnesium is included with the metals of the alkalies in the fifth group, on account of the solubilities of its salts in solutions of the salts of ammonium; in its properties it is intermediate between zinc and the metals of the alkaline earths. The metal decomposes water on boiling, but not in the cold; and its hydrate is a weaker base than the hydrate of calcium, as is evidenced by the decomposition of the hydrated chloride on heating, the formation of a basic carbonate, and the ease with which the latter may be converted into the oxide.

Potassium and *Sodium* decompose water in the cold, forming hydrates which are among the strongest bases known; their salts, and those of ammonium, are almost without exception (see tables) easily soluble in water.

Lithium shares the properties of the alkali metals with those of magnesium (*cf.* position in Mendelejeff's table), resembling the latter in the insolubility of its carbonate and phosphate, the former in the isomorphous relations of a few of its salts.

MAGNESIUM. $Mg = 23.82$.

OCCURRENCE.—*Ores*: magnesite; dolomite, $MgCa(CO_3)_2$; epsomite, $MgSO_4.7H_2O$; and spinelle, $MgAl_2O_4$. *Metallurgy*: the metal is obtained by electrolysis of the fused chloride, or by reduction of the latter with sodium. *In commerce*; metal; epsom salts, $MgSO_4.7H_2O$; magnesia, $Mg(OH)_2$; magnesia alba (basic magnesia carbonate); asbestos, $(Mg\ Ca)\ SiO_3$.

ATOMIC WEIGHT.—*Stoech. fig* : **16.0263** grm. magnesia
yielded 47.8015 grm. magnesium sulphate. *Specific heat*, 0.245.
Isomorphous relations : with zinc, iron, nickel, cobalt, and
manganese, in $MeSO_4.7H_2O$; with these, together with
copper, cadmium, mercury, and chromium in $MeSO_4.K_2SO_4.$
$6H_2O$; with calcium, zinc, iron, and manganese, in $MeCO_3$;
with zinc and iron in $MeAl_2O_4$.

The Compounds of Magnesium.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
Acetate .... $Mg(C_2H_3O_2)_2$	white	50 (12°)	very sol.	
Bromide .... $MgBr_2.6H_2O$	white	very sol.	very sol.	
Carbonate .... $MgCO_3$	white	0.025	insol.	$NaHCO_3$ cold, no ppt.
Chloride .... $MgCl_2.6H_2O$	white	130	367	
Chromate ...... $MgCrO_4$	white	sol.	very sol.	
Cyanide .... $Mg(CN)_2$	white	sol.	sol.	Dec. on evaporation.
Ferrocyan... $Mg_2Fe(CN)_6$	white	25	sol.	
Ferricyan.$Mg_3(Fe(CN)_6)_2$	white	sol.	very sol.	
Hydrate. .. ..$Mg(OH)_2$	white	s. sol.	s. sol.	Sol'n shows alkaline reaction.
Iodide. .... MgI_2	white	deliq.	deliq.	
Nitrate. .$Mg(NO_3)_2.6H_2O$	white	200	very sol.	
Oxalate .... MgC_2O_4	white	0.07(15°)	0.08	Insol. acetic acid.
Oxide ....MgO	white	0.001	insol.	
Phosphate .... $MgHPO_4$	white	s. sol.	s. sol.	
Sulphate.... $MgSO_4.7H_2O$	white	25.8 (0°)	71.4	Epsom salts.
Sulphide .... MgS	brown	s. sol.	dec.	
Sulphocyan..... $Mg(SCN)_2$	white	deliq.	very sol.	
Thiosulph . $MgS_2O_3.6H_2O$	white	125 (18°)	very sol.	
Amm. phosphate.........	white	0.005	insol.	$Mg(NH_4)PO_4.6H_2O.$

Sol. in tartrates : carbonate, hydrate, oxalate.
Sol. in ammon. chl.: carbonate, hydrate, oxalate, phosphate.

Magnesium is a malleable silver-white metal, *sp. gr.* 1.75,
m.p. 750°C. ; it oxidizes slowly in the air at ordinary temper-
tures ; heated, it burns to form the oxide MgO. It decom-
poses water slowly at 100°C.

Magnesium compounds, MgX_2; colorless in solution, except
when the acid is colored.

Magnesium phosphates, white. " Ordinary " sodium phos-
phate Na_2HPO_4 precipitates from concentrated solutions
of magnesium salts, $MgHPO_4$; from dilute solutions, $Mg_3(PO_4)_2$
only on heating ; from solutions containing ammonia and

ammonium salts, $MgNH_4PO_4$ (from very dilute solutions only on long standing or on rubbing the walls of the test-tube with a glass rod).

BLOWPIPE REACTIONS.—If the magnesium compound be first ignited, then moistened with cobalt nitrate, and ignited again, the mass assumes a pale rose-red color.

POTASSIUM. $K = 38.84$.

OCCURRENCE.—*Sources of potassium*: sylvine, KCl; carnallite, $KCl.MgCl_2.6H_2O$; wood ashes (carbonate). *Metallurgy*: reduction of the carbonate by ignition with carbon; also by electrolysis. *In commerce*: caustic potash, KOH; the bromide, iodide, chlorate, nitrate (saltpetre), cyanide, ferrocyanide, chromate, etc., etc.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
Acetate .... $KC_2H_3O_2$	white	deliq	deliq.	
Bromide ....KBr	white	· 25	100	
Carbonate......$K_2CO_3.2H_2O$	white	25	100	
Carbonate...........$KHCO_3$	white	1.	sol.	Bicarbonate.
Chloride ....KCl	white	32	57	
Chromate ....K_2CrO_4	yellow	50	60	
Cyanide ....KCN	white	very sol.	dec.	
Ferrocyan. $K_4Fe(CN)_6.3H_2O$	yellow	28	100	
Ferricyan ....$K_3Fe(CN)_6$	red	40	80	
Hydrate ....KOH	white	200	very sol.	
Iodide ....KI	white	120	200	
Nitrate.............KNO_3	white	25	200	
Oxalate............$K_2C_2O_4$	white	50	67	
Oxide ....K_2O	white	very sol.	very sol.	
Phosphate...........K_3PO_4	white	sol.	sol.	
Phosphate.........K_2HPO_4	white	very sol.	very sol.	
Sulphate .... K_2SO_4	white	12.5	25	
Sulphate ....$KHSO_4$	white	very sol.	very sol.	
Sulphide ....K_2S	white	very sol.	very sol.	
Sulphocyan .... $KSCN$	white	very sol.	very sol.	
Thiosulph.....$K_2S_2O_3.\frac{1}{2}H_2O$	white	very sol.	very sol.	
Tartrate ....$KHC_4H_4O_6$	white	1.2(25°)	6.6(100°)	Normal tart'te very sol.
Platinichloride	yellow	0.9(10°)	5.2(100°)	K_2PtCl_6
Pot. Antimonyl. Tartrate.. ...	white	7.	53	Tartar emetic.

ATOMIC WEIGHT.—*Stoech. fig.*: 210.85508 grm. silver required 145.70775 grm. potassium chloride to convert it into

silver chloride ; 487.6605 grm. potassium chlorate on reduction yielded 313.8175 grm. potassium chloride. *Specific heat*, 0.166. *Isomorphous relations* : with the other alkali metals, silver and thallium, in the alums ; with sodium and silver in $MeCl$; with ammonia in many salts and double salts.

SODIUM. $Na = 22.87$

OCCURRENCE.—*Sources of sodium* : rock salt, $NaCl$; sea water. *Metallurgy* : see potassium. *In commerce* : metal ; caustic soda, $NaOH$; washing soda, $Na_4CO_3 10H_2O$; baking soda $NaHCO_3$; common salt, $NaCl$; Chili saltpetre, $NaNO_3$; Glauber's salts, $Na_2SO_4.10H_2O$; " hypo," (sod. thiosulphate), $Na_2S_2O_3 5H_2O$; hypophosphite, $NaH_2PO_2.H_2O$; borax, $Na_2B_4O_7$; water-glass, $Na_2Si_4O_9$; bichromate, $Na_2Cr_2O_7.$ $2H_2O$; etc.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
SODIUM.				
Acetate ..$Na\ C_2H_3O_2 3H_2O$	white	33	200	
Borate ....$Na_2B_2O_7.12H_2O$	white	6	200	Borax.
Bromide.......$Na\ Br.4H_2O$	white	75	112	
Carbonate...$Na_2Co_3.10H_2O$	white	21	420	
Carbonate........$Na\ HCO_3$	white	10	dec.	
Chloride.............$Na\ Cl$	white	35	40	
Chromate $Na_2CrO_4...10H_2O$	yellow	sol.	sol.	
Bichromate $Na_2Cr_2O_7.2H_2O$	red	sol.	sol.	
Cyanide ....$Na\ CN$	white	sol.	sol.	
Ferrocyan......$Na_4Fe(CN)_6$	yellow	20	sol.	
Ferricyan .....$Na_3Fe(CN)_6$	red	20	80	
Hydrate ....$Na\ OH$	white	60	210	
Iodide..........$Na\ I.4H_2O$	white	185	300	
Nitrate....... ....$Na\ NO_3$	white	80	200	
Oxalate ....$Na_2C_2O_4$	white	4	4	
Oxide.... ....Na_2O	white	very sol.		
Phosphate ..*normal* (12H_2O)	white	20	sol.	
Phosphate ... ...*sec.* (12H_2O)	white	3	96	
Sulphate...........Na_2SO_4	white	5	42	
Sulphate.... ....$Na\ H\ SO_4$	white	very sol,	very sol.	
Sulphide.... .... Na_2S	white	sol.	sol.	
Sulphocyan........$Na\ SCN$	white	deliq.	deliq.	
Thiosulph...$Na_2S_2O_3.5H_2O$	white	102	very sol.	
Platinichloride.	red	very sol.	very sol.	$Na_2\ Pl\ Cl_6$
Pyroantimoniate..	white	insol.	insol.	$Na_2H_2Sb_2O_7.6H_2.O$

ATOMIC WEIGHT.—85.03122 grm. sodium chloride con-
verted 156.86206 grm. silver into silver chloride. *Specific heat,*
0.293. *Isomorphous relations*: with the other alkali metals, silver
and thallium, in the alums; with potassium and silver, in
$Me\,Cl$; with silver, in Me_2SO_4.

LITHIUM = 7.0.

OCCURRENCE.—*Ores*: lepidolite, or lithia mica, a complex
silicate; triphylline, a phosphate containing iron, etc.; found
also in many mineral waters. *Metallurgy*: by electrolysis of
the chloride. *In commerce*: carbonate, Li_2CO_3.

ATOMIC WEIGHT.—*Stoech. fig.*: 15.5533 grm. lithium car-
bonate, with dil. sulphuric acid gave 9.2414 grm. carbon
dioxide. *Specific heat*, 0.941. *Isomorphous relations*: with
the other alkali metals, silver and thallium, in the alums.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
Acetate.........$Li\,C_2H_3O_2$	white	350		
Bromide ... .$Li\,Br$	white	140	300	
Carbonate ....Li_2CO_3	white	0.1	1.5	
Chloride.......$Li\,Cl.2H_2O$	white	65	125	
Chromate... ......Li_2CrO_4	yellow	very sol.	very sol.	
Hydrate ....$Li\,OH$	white	s. sol.	s. sol.	
Nitrate...... ......$Li\,NO_3$	white	48	very sol.	
Oxalate...........$Li_2C_2O_4$	white	.7	sol.	
Phosphate ....Li_3PO_4	white	0.04	s. sol.	
Sulphate ......$Li_2SO_4.H_2O$	white	35	28	

AMMONIUM.

OCCURRENCE.—*Sources of ammonia*: at the present day
ammonia is obtained exclusively as a by-product in the
manufacture of coal gas. *In commerce*: "ammonia," solution
of NH_3 in water; sal-ammoniac, NH_4Cl; microcosmic salt,
$HNa(NH_4)PO_4 . 4H_2O$; carbonates; sulphate.

Nessler's test for ammonia : add potassium iodide (35 grm.) to a solution of mercuric chloride (13 grm.), until the precipitate at first formed is almost completely redissolved ; then add potash (100 grm.), let settle, and pour off the clear supernatant liquid (dilute to one litre). The solution so prepared is known as " Nessler's reagent," and with ammonia, or its salts, produces a brown precipitate, NHg_2I ; most delicate test for ammonia.

NAME.	Color.	Solubility in 100 parts cold water.	hot	Remarks.
Ammonia. . . . . NH_3	gas	87.5(0°)	19(56°)	Solubilities for 760 *mm.*
Acetate. . . . . . . $NH_4C_2H_3O_2$	white	deliq.	deliq.	
Bromide. . . . . NH_4Br	white	very sol.	very sol.	
Carbonate. . . . . $(NH_4)_2CO_3$	white	sol.	sol.	
Chloride. . . . . NH_4Cl	white	33	77	
Chromate. . . . . $(NH_4)_2CrO_4$	yellow	very sol.	dec.	
Cyanide. . . . . NH_4CN	white	sol.	very sol.	
Ferrocyan.$(NH_4)_4Fe(CN)_6$	yellow	sol.	sol.	
Ferricyan. $(NH_4)_3Fe(CN)_6$	red	very sol.	very sol.	
Iodide. . . . . NH_4I	white	deliq.	deliq.	
Nitrate . . . . NH_4NO_3	white	200	very sol.	
Oxalate . . . . $(NH_4)_2C_2O_4$	white	5	41	
Phosphate. . . $(NH_4)_2HPO_4$	white	20	sol.	
Sulphate. . . . . $(NH_4)_2SO_4$	white	77	98	
Sulphide . . . . $(NH_4)_2S$	colorless	sol.	sol.	In air forms polysulphides [yel.
Sulphocyan. . . . . . . NH_4SCN	white	very sol.	very sol.	
Thiosulph . . . . . $(NH_4)_2S_2O_3$	white	125	very sol.	$(NH_4)_2 PtCl_6$.
Platinichloride	yellow	0.67	1.25	$(NH_4)_3 PO_4$. 10MO_3.
Mag. Molybdate.	white	0.007	. . . .	[3H_2O

SEPARATION IN THE FIFTH GROUP.

Detection of Magnesium (*in the absence of lithium*). To the filtrate from Group IV add a little ammonia, enough ammonium chloride to redissolve any precipitate formed, and, lastly sodium phosphate.

Precipitate: magnesium ammonium phosphate; white.

Separation of Magnesium from Lithium: Prepare a neutral solution of chlorides, free from ammonia, as follows:—evaporate to dryness the filtrate from Group IV, ignite gently, dissolve the residue in dilute hydrochloric acid, evaporate to dryness again, and dissolve in a little water.

To the solution so obtained add ammonium oxalate, boil, and add acetic acid in excess.

Precipitate: magnesium oxalate, white.

Solution: lithium salts (precipitated by sodium phosphate).

Ammonia: salts of ammonium on boiling with potash evolve ammonia gas, recognized by its odor, by forming white fumes with hydrochloric acid, and by its action on litmus and on turmeric paper.

Sodium, potassium, and lithium are most easily detected by the colorations they impart to the non-luminous flame.

DETERMINATION OF THE ACIDS.

The method of grouping and analyzing the acids is identical with that already employed in the determination of the bases. As in the former case, the acids are divided into classes by their behavior with certain group reagents. This division, however, is much less complete than is that of the bases, and at best serves but to group the acids into a few large classes, each member of which must be tested for in a separate portion of the solution.

Before beginning with the wet tests involved in grouping the acids, it is advisable to subject a little of the solid substance to a preliminary examination, by heating it on platinum foil, and by warming it in a test-tube with strong sulphuric acid; whereby, in a majority of cases, valuable information as to the nature of the acids present may be obtained. A knowledge of the bases present is also of great service, as by consulting tables of the solubilities of the salts of the bases in question, it is often possible to greatly restrict the number of acids to be tested for. For example, if the salt submitted for analysis be soluble in water, all of those acids which form insoluble salts with the metals present are necessarily excluded.

If any bases other than the alkalis be present, they must first be removed, because of difficulties which their presence might introduce into the separation. This may conveniently be effected by precipitating with sodium carbonate, and filtering; after which the filtrate must be carefully neutralized before testing for the acids.

The substance to be analyzed may be brought into solution by the use of water alone, or of potash (for obvious

reasons acids are rarely employed).   In case it prove insoluble
in these solvents, it should be fused with sodium carbonate
(thus forming the soluble sodium salt of the acid), the fused
mass digested with hot water, the insoluble carbonate filtered
off, and the excess of sodium carbonate in the filtrate carefully
neutralized with dilute hydrochloric acid.

PRELIMINARY INVESTIGATION.

BEHAVIOR ON HEATING ALONE :

A small portion of the substance is cautiously heated on
platinum foil in the Bunsen flame : *blackening* indicates organic
substances.

BEHAVIOR ON TREATING WITH CONC. SULPHURIC ACID :

(*a*) Evolution of a colored gas :

Reddish brown, bromates, bromides, nitrites ; *pale yellow*,
chlorates, hypochlorites ; *violet*, iodides.

(*b*) Evolution of a colorless gas possessed of a distinct odor :

Odor of vinegar, acetates ; *hydrochl. acid*, chlorides ; *peach-
blossom odor*, cyanides, ferricyanides, ferrocyanides, sulphocy-
anides ; *hydrofluoric acid*, fluorides ; *nitrogen pentoxide*, nitrates ;
hydrogen sulphide, sulphides ; *sulphur dioxide*, sulphites, thiosul-
phates ; *odor of burnt sugar*, tartrates.

(*c*) Evolution of a colorless, odorless gas :

Carbonates, citrates, oxalates.

(*d*) No evolution of gas :

Arseniates, arsenites, benzoates, borates, chromates,
phosphates, salicylates, silicates.

DIVISION INTO GROUPS.

I. THE CALCIUM GROUP.—To the neutral solution, from which all bases but the alkalies have been removed, add calcium nitrate, if a precipitate appear, boil, cool thoroughly and filter.

  Precipitate : calcium salts of the acids of the first group ; those in brackets slightly soluble.

To the precipitate add acetic acid :—

  Solution, with evolution of gas: carbonate, sulphite.

  Solution : arseniate, arsenite, borate, citrate, phosphate, (tartrate).

  Residue, soluble in dil. hydrochl. acid : fluoride, (iodate), oxalate.

  Residue, insoluble in dil. hydrochl. acid : silicate, (sulphate).

II. THE SILVER GROUP.—To the filtrate from Group I add silver nitrate, filter.

  Precipitate : silver salts of the acids of the second group.

To the precipitate add nitric acid, and boil :—

  Solution : acetate, hypophosphite, sulphide, thiosulphate.

  Residue, insol. in ammonia : bromide (slightly sol.), iodide.

  Residue, soluble in ammonia : benzoate, bromate (bromide), chloride, chromate, cyanide, ferricyanide, ferrocyanide, hypochlorite, iodate, salicylate, sulphocyanate.

III. ACIDS WHOSE CALCIUM AND SILVER SALTS ARE SOLUBLE.—Chloric, nitric, nitrous, perchloric.

REACTIONS OF THE ACIDS.

ACETIC ACID, $C_2H_4O_2$.—All acetates are soluble in water (silver and mercurous acetates sparingly soluble).

Sulphuric acid, hot, conc.: characteristic odor of vinegar ; upon addition of a little alcohol, odor of ethyl acetate.

Ferric chloride : deep red color from formation of ferric acetate ; color not destroyed by mercuric chloride (*cf.* ferric sulphocyanate). On boiling with excess of acetate, basic ferric acetate (reddish brown) is precipitated.

ARSENIC ACID, H_3AsO_4.—All arseniates, except those of the alkali metals, insol. in water. For reactions, see page 61.

ARSENIOUS ACID, H_3AsO_3.—All arsenites, except those of the alkali metals, insol. in water (calcium and barium arsenites sparingly soluble). For reactions, see page 60.

BENZOIC ACID, $C_7H_6O_2$.—Colorless, glistening thin lamellæ or needles. Most of the benzoates soluble in water and in alcohol.

Sulphuric acid, conc.: brown colored solution, from which benzoic acid is precipitated by water.

Ferric chloride : in neutral solutions, flesh-colored precipitate—basic iron benzoate.

BORACIC ACID (metaboracic acid H_3BO_3).—All borates, except those of the alkali metals insol. in water. Heated to 160°C., metaboracic acid is converted into pyroboracic acid $H_4B_2O_7$.

Flame test : a fragment of a borate, moistened with a drop of conc. sulph. acid and a little alcohol, and ignited, green flame ; this may also be obtained by moistening first with conc. sulph. acid, then with glycerine, and igniting upon a platinum wire.

BROMIC ACID, $HBrO_3$.—All bromates soluble in water (silver, lead, and mercurous bromates sparingly soluble); on heating they liberate oxygen with formation of bromides.

Sulphuric acid, hot conc.: liberation of bromine.

Silver nitrate: white precipitate $AgBrO_3$, decomposed by hydrochl. acid with evolution of bromine (distinction from bromides).

Potassium iodide in acid solution: liberation of iodine (blue color with starch).

CARBONIC ACID $[H_2CO_3?]$.—Carbonates and bicarbonates of the alkali metals soluble in water, all others insoluble; those of the alkali earth metals soluble in water saturated with carbon dioxide. All acids decompose carbonates with effervescence; the carbon dioxide liberated may be recognized by the turbidity it produces in a drop of lime water on a glass rod.

CHLORIC ACID $HClO_3$.—All chlorates soluble in water. Heated they liberate oxygen with formation of chlorides (distinction from nitrates).

Sulphuric acid, conc: Evolution of green-yellow chlorous oxide, ClO_2. [Caution: explosive—only small quantities to be experimented with.]

Aniline sulphate, in acid solution, is immediately colored an intense blue by a fragment of a chlorate.

CHROMIC ACID, H_2CrO_4.—Chromates of the alkali metals, of magnesium, calcium, and zinc, soluble in water; strontium and mercuric chromates sparingly soluble; the others insoluble. For reactions, see page 89.

CITRIC ACID, $C_6H_8O_7$.—Citrates of the alkali metals soluble in water; those of iron, copper, and tin sparingly soluble; the others insoluble, but for the most part soluble in alkali citrates, with formation of double salts.

Sulphuric acid, conc.: Decomposition with liberation of carbon dioxide and carbon monoxide (inflammable). No charring, except on prolonged heating (distinction from tartrates).

Calcium hydrate: white precipitate of calcium citrate formed upon prolonged heating (distinction from tartrates).

FERRICYANIC ACID, $H_3Fe(CN)_6$.—Ferricyanides of the alkalies, of the alkaline earths, and of magnesium, soluble in water (barium ferricyanide sparingly soluble); other ferricyanides insol.

Sulphuric acid, hot, conc.: evolution of hydrocyanic acid (*q.v.*). The solution should be tested for iron.

Ferrous sulphate: dark blue precipitate (Turnbull's blue).

Ferric chloride: no precipitate, brown coloration.

FERROCYANIC ACID, $H_4Fe(CN)_6$.—Ferrocyanides of the alkali metals, and of magnesium, calcium, and strontium; soluble in water; all others insol.

Sulphuric acid, hot, conc.: evolution of hydrocyanic acid (*q.v.*), forming a solution containing iron.

Ferrous sulphate: light blue precipitate, becoming darker on standing.

Ferric chloride: deep blue precipitate (Prussian blue).

Cupric sulphate: red-brown precipitate.

HYDRIODIC ACID, HI.—Silver, lead, mercurous and mercuric iodides, insol. in water; all other iodides soluble, (except bismuth iodide, decomposed); the insol. iodides dissolve in excess of potassium iodide with formation of double salts.

Sulphuric acid, hot, conc.: liberation of iodine (violet vapors).

Oxidizing agents, *e.g.*, potassium dichromate in acid solution, liberation of iodine (blue color with starch, violet with carbon disulphide or coal oil).

Silver nitrate: light yellow precipitate, insol. in ammonia (distinction from chlorides and bromides).

Cupric sulphate: brownish white precipitate, (*Cu I*). Solution to be tested for free iodine.

HYDROBROMIC ACID, HBr.—Bromides of silver, lead, and mercury (*ous*), insol. in water; mercuric bromide slightly soluble; other bromides easily soluble.

Sulphuric acid, hot, conc.: liberation of bromine (brown fumes).

Oxidizing agents, e.g., potassium dichromate in acid solution, liberation of bromine (yellow color with starch, or with carbon disulphide or coal oil).

Silver nitrate, yellow white precipitate, sparingly soluble in ammonia, (distinction from chlorides).

HYDROCHLORIC ACID *HCl*, chlorides of silver and mercury (*ous*), insoluble in water; lead chloride sparingly soluble, the others easily soluble.

Sulphuric acid, hot, conc.: liberation of hydrochloric acid gas (colorless acrid fumes; white cloud with ammonia.)

Potassium dichromate and concentrated sulphuric acid : formation of chromyl chloride ; see page 88.

HYDROCYANIC ACID, *HCN*, cyanides of alkalies, alkaline earths, magnesium, and mercury soluble in water ; the others insoluble, often soluble, however, in excess of alkali cyanide with formation of double salts.

Sulphuric acid, hot, conc.: evolution of hydrocyanic acid gas (poisonous, colorless gas; with pungent, so-called " peach blossom " odor).

Prussian blue test : to a solution of a cyanide add a few drops each of potash, of ferrous sulphate, and of ferric chloride ; boil, and acidulate with dilute hydrochloric acid. Prussian blue is formed.

Sulphocyanate test : to a solution of a cyanide add a few drops of ammonium sulphide, heat gently in an evaporating dish until the solution becomes colorless, acidulate with dilute hydrochloric acid, and add ferric chloride—blood-red coloration.

HYDROFLUORIC ACID, *HF*.—Fluorides of the alkali metals, of silver, tin and mercury (*ic*), soluble in water; of copper, bismuth, cadmium, iron, and zinc, sparingly soluble ; those of the alkaline earth metals and of magnesium, insoluble.

Sulphuric acid, hot, conc. : evolution of hydrofluoric acid, recognized by its pungent odor and by its etching action upon glass. Caution !

HYPOCHLOROUS ACID, $HClO$.—All hypochlorites (except that of silver) are soluble in water. They are decomposed by dilute acids with liberation of free chlorine, which may be recognized by its odor, color, and bleaching action upon moist litmus paper.

Silver nitrate: white precipitate, silver hypochlorite; quickly decomposing into silver chloride and silver chlorate.

Aniline sulphate, in dilute sulphuric acid solution, upon addition of a fragment of a hypochlorite, blue coloration.

HYPOPHOSPHOROUS ACID, H_3PO_2.—All hypophosphites are soluble in water. Heated with nitric acid they form ortho-phosphates.

Cupric sulphate: heated to $70C°$, black precipitate of copper hydride; decomposed upon heating, or upon treatment with dil. hydrochl. acid.

Potassium permanganate, chromic acid, and a *solution of potassium iodide containing iodine*, are all reduced (decolorized) by hypophosphites.

Silver nitrate: black precipitate of reduced silver.

IODIC ACID, HIO_3.—Iodates of the alkali metals soluble in water; other iodates insol., or very sparingly soluble.

Sulphuric acid, hot, conc.: no evolution of iodine.

Ferrous sulphate and conc. sulphuric acid: liberation of iodine (see hydriodic acid).

NITRIC ACID, HNO_3.—All nitrates are soluble in water.

Brown ring test: one centimetre each of the solution of a nitrate and of ferrous sulphate solution are mixed in a test-tube and conc. sulphuric acid added, allowing it to fall along the wall of the tube: at the boundary between the two liquids a brown ring or coloration will be observed, arising from the solution of nitric oxide in ferrous sulphate.

Phenyl sulphate (1 part phenol, 4 parts conc. sulph. acid, and 2 parts water): brown-red coloration, becoming yellow or green upon addition of ammonia.

NITROUS ACID, HNO_2.—All nitrites are soluble in water —silver nitrite sparingly soluble.

Brown ring test: obtained by the action of ferrous sulphate on a nitrite, without addition of sulphuric acid (distinction from nitrates, *q.v.*).

Potassium iodide with dil. sulph. acid: liberation of free iodine (see hydriodic acid).

OXALIC ACID, $C_2H_4O_2$.—Oxalates of the alkali metals and of magnesium and iron (ferric), soluble in water; chromic and stannic oxalates, sparingly soluble; the others, insoluble.

Sulphuric acid, hot, conc.: evolution of carbon dioxide and carbon monoxide (inflammable).

ORTHOPHOSPHORIC ACID, H_3PO_4.—Di and tri-metallic phosphates, with the exception of those of the alkali metals, insoluble in water; mono-metallic phosphates, usually somewhat soluble.

Ammonium molybdate: mix in a test-tube one cubic centimetre of ammonium molybdate solution, with one drop of the solution of the phosphate, and add dilute nitric acid until the precipitate at first formed (MoO_3) is redissolved. The liquid assumes a yellow color, and on warming (not boiling!) a canary-yellow precipitate of ammonium phosphomolybdate $(NH_4)_3PO_4.12MoO_3$ is formed.

"Magnesia mixture" (prepared by the addition of ammonia to a solution of magnesium sulphate containing ammonium chloride in sufficient quantity to prevent the formation of a precipitate): white crystalline precipitate of magnesium ammonium phosphate.

Silver nitrate: yellow precipitate, Ag_3PO_4; (distinction from pyrophosphoric acid).

PYROPHOSPHORIC ACID, $H_4P_2O_7$.—Pyrophosphates of the alkali metals soluble in water; all others insol. Upon heating in acid solution, pyrophosphates are converted into orthophosphates.

Ammonium molybdate: no precipitate (*cf.* orthophosphoric).
"Magnesia mixture": no precipitate (*cf.* orthophosphoric).
Silver nitrate: white precipitate.

SALICYLIC ACID, $C_7H_6O_3$; colorless four-sided prisms, or long needle-like crystals, odorless, but possessed of a sour-sweet taste. Salicylic acid and its salts are sparingly soluble in cold water, easily soluble in hot water and in alcohol.

Ferric chloride: intense violet coloration.

Alcohol and concentrated sulphuric acid on warming: odor of wintergreen.

Heated with lime: odor of phenol. (carbolic acid).

SILICIC ACID [$HSiO_3$?].—Silicates of the alkali metals are soluble in water, all others insol.

Hydrochloric acid: decomposition with separation of jelly-like mass, insol. when once dried.

Silica skeleton: If a small fragment of a silicate be dissolved in the microcosmic salt bead, the silicic acid is liberated and floats undissolved in the bead, which forms an opalescent glass upon cooling.

SULPHURIC ACID, H_2SO_4.—Sulphates of barium, lead, and strontium, insol. in water; of silver, calcium, and mercury (ous), sparingly soluble; the others, soluble.

Barium chloride: white precipitate ($BaSO_4$) insoluble in all acids.

ALL ACIDS CONTAINING SULPHUR.—*B. B. on C.* with carb. soda form sodium sulphide. The fused mass, moistened and placed on a silver coin, produces a black stain. "Silver coin test."

SULPHURETTED HYDROGEN, H_2S.—Sulphides of the alkalies, of the alkaline earths, and of magnesium, soluble in water; aluminium and ferric sulphides decomposed; all other sulphides insol.

Sulphuric acid, hot, conc.: evolution of sulphuretted hydrogen; (odor; lead acetate paper blackened).

*Potassium nitroprusside** and potash solution: violet red coloration, which disappears on standing.

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*Prepared by heating potassium ferrocyanide with nitric acid, and neutralizing with potash.

SULPHUROUS ACID, $[H_2S.O._3?]$—Alkali sulphites, soluble; all others insoluble in water.

All acids: evolution of sulphur dioxide (odor).

Barium chloride: white precipitate, soluble in dilute hydrochloric acid. If to this solution a little dilute nitric acid be added, insoluble barium sulphate is formed upon heating.

Silver coin test: see page 126.

SULPHOCYANIC ACID, $(HCNS)$—Sulphocyanates of the alkalies, alkaline earths, magnesium, iron, manganese, zinc, cobalt, copper, and mercury, (*ic*) soluble in water, all others insoluble.

Ferric chloride: blood red coloration, decolorized by mercuric chloride (distinction from acetic acid), by arsenious acid, by oxalic acid, and by sodium acetate (color restored by hydrochloric acid).

TARTARIC ACID, $\dot{C}_4H_6O_6$.—Tartrates of alkali metals, manganous, ferric, cobalt, stannous, and antimonious tartrates, soluble in water; acid tartrates of potassium, ammonium, and calcium, sparingly soluble; all other tartrates insoluble in water, but often dissolved in excess of alkali tartrates with formation of double tartrates.

Sulphuric acid, hot, conc.: charring, and odor of burnt sugar.

Silver mirror: Dissolve the tartrate in ammonia, add silver nitrate, and allow to stand for a few minutes in a warm place. The inside of the test tube becomes coated with metallic silver.

THIOSULPHURIC ACID, $H_2S_2O_3$.—Thiosulphates of silver, lead, and barium, sparingly soluble in water; all others easily soluble. The insoluble thiosulphates are, in most cases, easily dissolved by excess of alkali thiosulphates.

All acids: decomposition with evolution of sulphur dioxide, and precipitation of sulphur (distinction from sulphites).

Silver nitrate: white precipitate, silver thiosulphate, gradually becoming black from formation of silver sulphide.

Potassium permanganate; *iodine solution*: both decolorized.

Silver coin test: see page 126.

THE ALKALOIDS.

The term "alkaloids" is restricted in chemistry, to a somewhat extensive class of organic bases, which are usually found, uncombined, in nature, in certain plants. They contain carbon, hydrogen, oxygen, and nitrogen in varying proportions, and are related chemically to the pyridine and quinoline bases. Often grouped with the alkaloids, on account of their physiological action, are substances which, chemically, are widely different, *e.g.*, glucosides, albuminoids, etc.; a few of the more common of these are included in a supplementary list at the end of the alkaloids proper.

The alkaloids are colorless compounds possessed of bitter taste and characteristic physiological action. They are usually insoluble in water, readily soluble in acids, with which they form well defined salts. From their solutions most alkaloids may be precipitated by potassium mercuric iodide, by phosphomolybdic acid, and in some cases by dilute potash. The first two precipitates vary in color from white to yellow and are insoluble in dilute acids.

No satisfactory and complete method for grouping the alkaloids has been devised. The following scheme, proposed by Fresenius, will be found of assistance in roughly subdividing them, after which each member of the sub-groups must be tested for separately.

DIVISION INTO GROUPS.

VOLATILE : coniine, nicotine, (recognized by their distinctive odors).

NON-VOLATILE : brucine, morphine, strychnine, etc.
  (a) To a portion of the solution of the non-volatile alkaloid, add potash to slight alkaline reaction ; allow to stand five minutes, and, if a precipitate appear, add potash to strongly alkaline reaction.
  The precipitate dissolves : (atropine*), cocaine, morphine.
  The precipitate is insoluble : aconitine, brucine, cinchonine, narcotine, quinine, strychnine, veratrine.
  (b) To another portion of the solution add a few drops of dilute sulphuric acid, neutralize with concentrated solution of bicarbonate of soda, and allow to stand fifteen minutes.
  Precipitate : cinchonine, narcotine, quinine.
  No precipitate : brucine, strychnine, veratrine.

*Precipitated by potash from concentrated solutions only.

REACTIONS OF THE ALKALOIDS.[*]

ACONITINE, $C_{33}H_{43}NO_{12}$,— Colorless powder, difficultly soluble in water, easily soluble in acids and alcohol.

Sulphuric acid, conc. : solution with yellowish brown coloration, which becomes bright yellow upon addition of dilute nitric acid.

ATROPINE, $C_{17}H_{23}NO_3$.—Lance-shaped colorless crystals ; difficultly soluble in cold water, easily soluble in alcohol and in acids.

Sulphuric acid, hot, conc. : odor of orange blossoms.

BRUCINE, $C_{23}H_{26}N_2O_4.4H_2O$.—Colorless, prismatic crystals ; difficultly soluble in water, easily soluble in alcohol and in dilute acids.

Sulphuric acid, conc., containing nitric acid :[†] intense red coloration.

Nitric acid, conc. (sp. gr. 1.4) : blood-red coloration, quickly changing to yellowish red.

Chlorine or bromine water : pink coloration, yellowish brown on addition of ammonia.

CINCHONINE, $C_{19}H_{22}N_2O_1$.—Transparent, lustrous prisms, or white powder ; insoluble in water, soluble in alcohol and in acids.

Potassium ferrocyanide flocky-white precipitate, soluble in excess (distinction from quinine).

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[*] Alkaloids are sometimes arranged as follows : (a) Volatile : nicotine, coniine ; (b) Alkaloids of opium : cocaine, codeine, morphine, narcotine, papaverine ; (c) Strychnine and related compounds : brucine, strychnine ; (d) Quinine and related compounds : aconitine, atropine, cinchonine, colchicine, quinine, veratrine.

[†] This solution (recommended by Erdmann) is prepared as follows : to 100 c.c. water add 5 drops nitric acid, *sp. gr.* 1.25 ; to 20 c.c. conc. sulph. acid add 10 drops of this dilute solution of nitric acid.

Chlorine or bromine water, then ammonia : white precipitate.

COCAÏNE, $C_{17}H_{21}NO_4$.—Colorless prisms; difficultly soluble in water, soluble in alcohol and in acids.

Ammonia : white precipitate, soluble in excess.

CODEÏNE, $C_{18}H_{21}NO_3.H_2O$.—Colorless, rhombic crystals; difficultly soluble in water, easily soluble in alcohol and in acids.

Sulphuric acid conc., containing nitric acid : blue coloration.

Nitric acid conc. : yellow solution.

COLCHICINE, $C_{22}H_{26}NO_6$ —Yellowish-white resinous material, soluble in water and in alcohol.

Nitric acid conc. : violet coloration; upon addition of water, yellow.

Sulphuric acid conc. : cold, yellow coloration ; upon heating, red. If the sulphuric acid contain a trace of nitric acid, the color of the solution changes gradually from green to yellow.

CONÏNE, $C_8H_{17}N$.—Transparent, oily liquid, possessed of a nauseating odor and taste ; difficultly soluble in water, easily soluble in alcohol.

Potassium mercuric iodide : resinous precipitate, becoming crystalline on standing.

Chlorine water : turbidity (distinction from nicotine).

MORPHINE, $C_{17}H_{19}NO_3.H_2O$.—Colorless, clinorhombic prisms; difficultly soluble in water, easily soluble in alcohol and in acids.

Nitric acid, conc. : orange yellow coloration.

Ferric chloride : deep blue coloration.

NARCEÏNE, $C_{23}H_{29}NO_9.2H_2O$.—Long glistening needles, difficultly soluble in cold, easily in hot water or alcohol.

Sulphuric acid conc.: solution with brown color; with excess of acid, bright yellow.

Iodine, dissolved in potassium iodide solution : the solid alkaloid colored blue (distinction from all other opium alkaloids).

NARCOTINE, $C_{22}H_{23}NO_7$.—Colorless, lustrous prisms; insoluble in water and in alcohol, slightly soluble in acids.

Sulphuric acid conc., containing nitric acid : orange yellow coloration, changing to red and finally to violet.

Bromine water : yellowish green coloration; upon addition of ammonia, yellowish red.

NICOTINE, $C_{10}H_{14}N_2$.—Colorless oil; soluble in water, in alcohol and in acids.

Nitric acid conc.: red coloration.

Potassium mercuric iodide : resinous precipitate, becoming crystalline on standing.

PAPAVERINE, $C_{20}H_{21}NO_4$.—Colorless, needle-shaped crystals, insoluble in water and in cold alcohol, soluble in warm alcohol and in acids.

Sulphuric acid conc. : cold, no coloration, heated, deep violet blue.

PIPERINE, $C_{17}H_{19}NO_3$.—Glassy four-sided prisms, insol. in water, fairly soluble in alcohol.

Sulphuric acid conc. : solution with yellow color, becoming dark brown and finally greenish-brown on standing.

QUINIDINE, $C_{20}H_2 N_2O_2$.—Glistening four-sided prisms, very difficultly soluble in water, easily in alcohol; reactions as under quinine, with one exception, viz :—

Potassium iodide : in neutral solutions, white powdery precipitate.

QUININE, $C_{20}H_{24}N_2O_2$.—White amorphous powder, difficultly soluble in water, easily soluble in acids. The solutions of quinine and its salts are phosphorescent.

Bromine water and then ammonia : green, flocky, precipitate, soluble in excess of ammonia to form emerald green solution ; neutralized with dilute hydrochloric acid, the solution becomes blue, and with excess of acid, violet or red.

Potassium ferrocyanide : dark red coloration.

STRYCHNINE, $C_{21}H_{22}N_2O_2$.—White glistening rhombic prisms, very difficultly soluble in water and in alcohol, easily soluble in dilute acids.

Sulphuric acid conc. : dissolves strychnine to form a clear solution. If to a small portion of this solution a fragment of potassium dichromate be added, a violet coloration, surrounding the dichromate, may be observed. This coloration is produced also (but less distinctly) by potassium permanganate, and by red lead.

Potassium ferricyanide : yellowish green coloration.

THEBAÏNE, $C_{19}H_{23},NO_3$.—White quadratic scales, insol. in water, easily in alcohol and in acids.

Sulphuric acid conc. : solution with blood red color, gradually becoming yellowish red.

Ferric chloride : no color reaction (distinction from morphine).

Nitric acid, sp. gr. 1.4 : solution with yellow color.

VERATRINE, $C_{32}H_{49}NO_9$.—Colorless prisms ; insol. in water, soluble in alcohol and in acids.

Sulphuric acid conc. : yellow coloration, becoming bright red on standing. Upon addition of bromine water this solution becomes purple.

Hydrochloric acid conc. : colorless solution cold, colored deep red upon boiling.

CAFFEÏNE OR THEÏNE, $C_8H_{10}N_4O_2H_2O$.—White, glistening, silky needles ; insol. in alcohol, soluble in water and in acids.

Chlorine or bromine water evaporated to dryness with a caffeine solution, and the reddish-brown mass moistened with ammonia : violet coloration.

DIGITALINE.—White, amorphous powder ; insol. in water, easily soluble in alcohol.

Sulphuric acid conc. : brown solution ; on standing, dark red ; with bromine water this solution gives a beautiful violet-red coloration.

PICROTOXINE, $C_{15}H_{16}O_6H_2O$.—White, glistening, four-sided prisms, or needles ; easily soluble in water, and in alcohol ; insol. in dilute acids.

Sulphuric acid conc.: golden yellow coloration ; upon addition of potassium bichromate, violet, and then green.

SALICINE, $C_{13}H_{18}O_7$.—White, glistening needles or lamellae ; easily soluble in alcohol and in water.

Sulphuric acid, conc. : colors salicine blood red without dissolving it.

Nitric acid conc. : colorless solution, cold ; yellow upon heating.

TABLE FOR THE DETECTION OF A SINGLE ACID.

I. To a portion of the Neutral Solution add Barium Chloride.

White precipitate, insol. in hydrochloric acid : *silicate, sulphate.*

White precipitate, soluble in hydrochloric acid : *borate, carbonate (effervescence), phosphate, sulphite (odor of sulphur dioxide), tartrate, thiosulphate, (separation of sulphur).*

Yellow precipitate, insol. in acetic acid : *chromate.*

White precipitate, insol. in acetic acid : *oxalate.*

II. To another portion of the solution add Silver Nitrate.

Precipitate, soluble in dil. nitric acid and in ammonia : white, *borate, carbonate, oxalate, silicate* ; yellow, *arsenite, phosphate* ; red, *arseniate* ; dark red, *chromate.*

Precipitate, insol. in dilute nitric acid, but soluble in ammonia : white, *chloride, cyanide, ferrocyanide (difficultly soluble), hypochlorite, sulphocyanate ;* yellow, *bromide (difficultly soluble)* ; orange red, *ferrocyanide.*

Precipitate, insol. in dilute nitric acid and in ammonia : white, *(ferrocyanide) ;* yellow, *(bromide), iodide* ; black, *sulphide,* (soluble in concentrated nitric acid).

III. Acids not precipitated by Barium Chloride or Silver Nitrate.

Brown ring test (page 124) : *nitrate, nitrite.*

Reaction with sulphuric acid (page 121) : *chlorates.*

*For the method of bringing the substance to be analyzed into solution, and for preliminary examination, see page 118.

MENDELEJEFF'S TABLE.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
R_2O	RO	R_2O_3	RO_2 RH_4	R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	RO_4
H 1.							
Li 7.0	Be 9.0	B 10.8	C 11.91	N 13.95	O 15.88	F 18.9	
Na 22.87	Mg 23.8	Al 26.9	Si 28.2	P 30.8	S 31.82	Cl 35.19	
K 38.84	Ca 39.7	Sc 43.8	Ti 47.8	V 50.8	Cr 51.8	Mn 54.5	Fe 55.6 · Co 58.4 Ni 58.3 Cu 63.1
	Zn 64.8	Ga 69.6	Ge 71.9	As 74.5	Se 78.5	Br 79.36	
Rb 84.8	Sr 87.0	Y 88.5	Zr 90.0	Nb 93.2	Mo 95.3		Ru 100.9 Rh 102.2 Pd 105.8 Ag 107.12
	Cd 111.2	In 113.0	Sn 117.2	Sb 119.0	Te 124.4	I 125.90	
Cs 132.0	Ba 136.4	La 137.5					
		Er 165.0					
				Ta 181.1	W 183.0		Os 189.3 Ir 191.5 Pt 193.33 Au 195.7
	Hg 198.8	Tl 202.7	Pb 205.4	Bi 207.3			
			Th 230.7		U 237.6		

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